THE MANUFACTURE OF ACIDS AND ALKALIS
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Completely Revised and Rewritten under the Editorship of
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VOLUME III

The Concentration of Sulphuric Acid

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THE CONCENTRATION
OF
SULPHURIC ACID

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EDITOR'S PREFACE

THE first English edition of Lunge's *Sulphuric Acid and Alkali* appeared in 1879. Since that date the book has been revised and extended in subsequent editions until, with the companion volumes on *Coal Tar and Ammonia*, it extended to nine volumes, covering most of the heavy chemical industries of Britain. A supplementary volume on Sulphuric and Nitric Acids by Dr Lunge in 1917 marked the end of his long labours in this field, and he informed the publishers that he could no longer undertake the preparation of new editions. The mere compilation of the volumes which he wrote would be in itself a wonderful achievement, but Dr Lunge's place in the history of chemical industry is due still more to the fact that he played a leading part in the discoveries and improvements which built up the industries of which he wrote.

By a curious coincidence, the end of Dr Lunge's long literary labours came just as the processes which he originally described died out. The Hargreaves process has gone, in this country at least; the Leblanc process is dying, if not actually dead already; even the chamber process for sulphuric acid has now a competitor that threatens to become a rival.

The volumes written by Dr Lunge have escaped a common criticism of factory managers that books give only an outline of a manufacturing process; indeed the only criticism has been that Dr Lunge's books gave almost too much detail. It may, however, be realised how important is a detail relating to a matter involving a possible saving of only one-tenth of one per cent., when it is pointed out that this small economy in the manufacture of sulphuric acid would mean a saving of thousands of pounds, since the value of the sulphuric acid manufactured annually in Great Britain alone amounts to several million pounds.

Each new edition of this series has been an expansion and extension of that which preceded it, fuller treatment being accorded to subsidiary manufactures as they increased in commercial importance, until the name *Sulphuric Acid and Alkali* became a cover for what was practically an encyclopedia of the heavy chemical industries.

The last arrangement into volumes and parts was largely fortuitous, having arisen from uneven growth of knowledge and commercial development in different branches, and as this appeared to be a favourable opportunity for instituting a new arrangement, it was decided to sub-divide the work into sections more in accord with modern developments. The last few years have brought with them so many changes in the chemical industries that the revision required in most of the volumes will involve such drastic recasting that the new edition will be more a new book than a revised edition.

It is doubtful if any one man could take up Dr Lunge's task of describing adequately all the industries now dealt with in these volumes, and it is certain that few would care to attempt it. Each volume will therefore be on a special subject and dealt with by a separate author who is responsible for that volume, and is given a wide discretion in his treatment of the subject.

The editor trusts that these united efforts will produce a new edition worthy of the great tradition which Dr Lunge has established.

The editor will be pleased to consider for publication in this series any manuscripts or original work on this or allied subjects.

A. C. C.

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AUTHOR'S PREFACE

ADVANTAGE has been taken of the opportunity afforded by the publication of a new and enlarged edition of Dr Lunge's treatise to revise completely the section dealing with the concentration of sulphuric acid, and to issue it in the form of a separate volume.

For the sake of completeness, and in order to trace the historical development of the subject, a short description of some of the earlier plants is included, but the great proportion of the text is composed of entirely new matter. Not only is a description given of all the newer and more economical types of plant which have been evolved by practical experience during the past decade, but the theoretical principles underlying the various processes are treated in greater detail than formerly.

The concentration of sulphuric acid was one of the earliest problems which the Chemical Engineer was called upon to solve during the great war of 1914-1918, and the necessity for dealing with the huge quantities of weak acid produced in the manufacture of explosives directed attention towards the development of units of large capacity, especially in the Government factories. No fundamentally new types of plant were evolved, but progress followed along well-defined lines. Much valuable experience and data have been obtained, however, from these plants, which are described in the text.

In conclusion, the Author acknowledges, with pleasure, the co-operation and help he has received from many sources in the preparation of the volume. A large amount of the statistical information is derived from the Chief Alkali Inspector's Reports, and from the Reports of the Factories Branch of the Department of Explosives Supply of the Ministry of Munitions. Special thanks are due to—Mr W. Macnab for permission to abstract from the Technical Records of Explosives Supply, Ministry of Munitions; Professor A. W. Porter for the tables and information on the Thermal properties of sulphuric acid; Mr W. G. MacKellar, United Alkali Co., Glasgow, and Mr C. S. Imison, United Alkali Co., Widnes, for valuable help in the description of the modern Kessler plant.

JOHN WILFRID PARKES.

DUBLIN, 1923.

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THE CONCENTRATION OF SULPHURIC ACID

CHAPTER I

INTRODUCTION

SULPHURIC acid, as obtained directly in the chambers (*i.e.*, from 106° Tw. to 130° Tw.), is concentrated sufficiently for many technical purposes; and where the acid is used for such purposes at the same works, its further concentration is, of course, unnecessary. This is the case, for instance, in several large industries having their own vitriol works, such as the manufacture of superphosphates and of sulphate of ammonia.

For higher strengths of acid up to 144° to 152° Tw., the acid from the Glover tower is employed wherever possible, as no cost is incurred in the process of concentration in this tower. By diluting Glover tower acid with the requisite amount of chamber acid, any acid can be obtained readily of strength intermediate between 130° and 144° Tw. For example, in the manufacture of sulphate of soda, acid of 132° to 133° Tw. is employed usually when working with rock salt; and acid of 138° to 140° Tw. when working with common salt (white). For some uses of sulphuric acid, however, the acid passed through the Glover tower is not suitable, and other forms of concentrating apparatus must be employed.

The manner in which sulphuric acid is concentrated depends on the strength of acid desired, and on the material of the concentrating vessel. Acid up to 144° Tw., or even up to 152° Tw., acts very little upon lead, even when hot; so long as the acid has not to be stronger than 144° Tw., lead vessels are used nearly always where it cannot be made in a Glover tower. They offer the advantage that the vessels can be made of any size, and that when they are worn out the lead can be melted down easily and used over again. It is not advisable to carry the concentration in lead pans above 144° Tw., because, beyond that point, the lead is much acted upon; in no case can lead pans be used beyond 152° Tw., because the boiling point of the acid approaches too nearly the temperature at which lead begins to soften, and because the acid then acts too strongly upon it (see p. 72, also Vol. I., p. 224).

The lead pans may be constructed in various ways according to whether they are heated (1) by direct fire from the top (see p. 45), (2) from the bottom (see p. 52), (3) by steam (see p. 66), or (4) by the waste heat of the pyrites burners (see p. 57).

In the Glover tower it is possible to attain a higher degree of concentration than in the lead pans, as the leadwork is protected by the brick lining so as to be acted upon very slightly. The acid does not come directly into contact with the lead, but only with the lining and packing of the tower, and arrives at the bottom with an average temperature of 130° C., so that even the bottom of the tower (which is made of extra heavy lead) is not acted upon sensibly. (Recently Glover towers have been erected entirely in acid-resisting brickwork.[1])

Manufacturers who work their Glover tower with hot gases from rich ores, and get their chamber acid up to 120 to 130° Tw. can attain a concentration of 150 to 152° Tw., and in some cases 156 to 160° Tw. can be reached. The latter is the exception, and always dangerous to the tower; if it were not so, the concentration by hot kiln gas in the Glover tower (of course modified to some extent) would be the cheapest plan for the final concentration of the acid, because then the escaping gases go into the chambers and are not lost at all. Concentration beyond the point attained in lead pans or in the Glover tower is a much more difficult task, involving incomparably more expense than the first concentration, and requiring apparatus of special construction. For many purposes, however, sulphuric acid of the highest possible strength is essential; for instance, the purification of mineral oils (petroleum, paraffin, etc.), and of benzol; the refining of gold and silver;

the production of nitro-cellulose, nitro-glycerine, nitro-benzene, nitro-toluene, and other nitro bodies; the production of sulphonic acids, and in the manufacture of resorcinol and alizarine; for dissolving indigo and for innumerable other purposes in the dye industry. In many cases an acid containing 93 to 94 per cent. H_2SO_4 will do. For making nitro compounds especially, however, an acid of greater strength is required (96 to 97 per cent.). For some purposes an acid as nearly as possible 100 per cent.—*i.e.*, monohydrate sulphuric acid—is required, and is made by adding fuming sulphuric acid (oleum) to ordinary sulphuric acid.

This is, however, another consideration which induces the manufacturer to incur the great expense and trouble of concentrating the acid made for sale as highly as possible, even in cases where the consumer, not requiring it of such strength, must himself dilute before using it, namely the greater expense of packages and cost of transit for the same weight of real acid in the dilute, as compared with the concentrated state.

Furthermore, in the manufacture of many chemicals and explosives, large quantities of weak sulphuric acid are produced, which require to be concentrated before they can be used over again.

Outline of the Processes used in Concentration.

Concentration in Glass Retorts.—At first glass retorts were the only available apparatus for the preparation of high strength sulphuric acid, and these could be obtained only of comparatively small size and inferior quality. They were set mostly in "galley furnaces," a long double row of retorts being heated by a fireplace at one end; thus the retorts near the fire were much more heated than those more distant, and were finished much sooner, or even overheated before the more distant retorts had been fired sufficiently. Owing to the inferior quality of the retort, and also to unsuitable setting (each retort was either put into a metal pot with some sand between, or protected from the direct flame by a covering of clay), there was always much breakage, combined not only with loss of acid but also with the sudden evolution of suffocating vapours. The cracking of the retorts was induced especially by a cold draught getting at them; and, since in that case the workmen had to save themselves instantly from the vapours by leaving the room, frequently the cracking extended to all the retorts. In addition the expenditure of time, wages, and fuel in this process was very great, in spite of improved retorts and better methods of setting and working (see p. 75).

Concentration in Platinum Stills.—There was always, therefore, an inducement to discover some other material than glass for the concentration of sulphuric acid. As soon as Wollaston's process of welding spongy platinum into ingots and plates was known, platinum was employed for this purpose, in spite of its high price and the difficulty of manipulating it. The first platinum still appears to have been made in 1809 in London, and weighed 423 oz.[1] Later on platinum stills weighing from 66 lb. to 112 lb. were made, holding from 4 to 6 tons of vitriol. The platinum vessels made by Wollaston's process were often porous and unsound, so that acid oozed through; and blisters and rents appeared frequently, which had to be soldered up with gold. The platinum stills, therefore, gave much dissatisfaction until Ste.-Claire Deville introduced the method of melting platinum in large masses by means of the oxygen blow-pipe in furnaces made of quicklime, by which sound ingots of platinum weighing 2 cwt. are obtained. With the oxy-hydrogen flame, also, the joints could be made with platinum itself instead of gold.

Platinum vessels were used extensively for the final concentration of sulphuric acid, because of the ease, safety, and large amount of work which could be carried on in them, and because it was thought (erroneously) that they would last indefinitely. When, however, attention was drawn to the fact that platinum is acted upon gradually by sulphuric acid, and that thus the large capital expended on the stills not only involves heavy permanent charges for interest but has to be written off gradually altogether, other forms of concentrating plant were adopted.

Improved and more economical methods of concentration have been developed along the following lines.

Concentration in Iron Pans.—The ever-increasing cost of platinum and the liability of glass to breakage, led to the employment of iron vessels (1882) for the final concentration of sulphuric acid, as cast iron resists the action of strong acid, although attacked by weaker acid (90 to 92 per cent. H_2SO_4).

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[1] *Chem. News*, 38, 43.

Concentration in Cascade Plants.—A new method of concentration was introduced (*circa* 1890) by the use of porcelain dishes, arranged in the form of a cascade, down which acid flows, and is heated by a current of hot gases from a fire. This system was adapted particularly for concentrating the acid from lead evaporating pans (144° Tw.) up to 92 to 93 per cent. H_2SO_4, at which strength it was fed into the cast iron concentrating pans. Improvements have been made from time to time by the introduction of porcelain and enamelled iron beakers, vitreosil basins, and of vessels made of acid-resisting ferrosilicon alloys (tantiron, ironac, narki, etc.), so that the cascade system of concentration has found extensive application in all parts of the world.

The Kessler Plant.—Many attempts were made to concentrate sulphuric acid by bringing hot fire gases in direct contact with the acid, but the processes of Kessler (1891) and Gaillard (1906) have alone achieved industrial success. In the Kessler plant hot gases from a coke producer are drawn over the surface of a shallow layer of acid in a flat volvic stone dish (the saturex), and then through a series of superimposed trays luted with acid (recuperator). The weak acid to be concentrated is introduced into the top tray, and, passing downwards through the trays to the bottom dish or saturex, meets the hot gases on its way. The concentration of the acid takes place in a regular manner throughout the system, and it leaves the saturex in a highly concentrated condition. The system has been adopted universally, and is excellent for moderate outputs.

The Gaillard Plant.—Gaillard introduced an entirely new principle in the atomising of the acid in the form of a fine spray down an empty tower, up which hot gases from a coke producer are ascending. Under these conditions, the contact between the acid and the hot gases is as intimate as possible, and concentration takes place regularly throughout the tower, so that the acid arrives at the bottom of the apparatus in a highly concentrated condition, and the gases, which enter the base at a red heat, are reduced considerably in temperature when they leave the top of the tower. The system has found extensive application for the production of large quantities of strong acid, and especially for the concentration of the waste acids from the manufacture of explosives.

Various modifications of the Kessler and Gaillard plants have been made, and these will be described subsequently in the text, together with other apparatus of special construction.

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CHAPTER II

THE PROPERTIES OF ORDINARY CONCENTRATED SULPHURIC ACID

THE strongest acid obtainable by boiling down ordinary pure sulphuric acid contains a quantity of water, which is not stated alike by different observers (Marignac, Pfaundler, Roscoe, Dittmar, Lunge, and Naef, etc.). The statements vary from 97·86 to 98·99 per cent. H_2SO_4, but Lunge's figure of 98·3 per cent. is usually accepted as correct. This *distilled sulphuric acid* solidifies a little below 0°; but it shows superfusion in a very high degree. It boils at 338° (Marignac); 315° to 317° (Pfaundler and Polt); but the latter figure is considered unreliable, and the acid probably contained a little more water. If boiled at atmospheric or lower pressures, the acid bumps violently, which can be avoided by putting in bits of platinum wire or foil; or, according to Dittmar, still better by conducting a slow current of air through it during the boiling. This acid of 98·3 per cent. is an acid of maximum boiling point (330°), as shown by Knietsch[1]; below this water or dilute sulphuric acid; above this sulphuric anhydride is volatilised, until, in either case, the constantly-boiling acid of 98·3 per cent. is reached. The vapour pressure measured at 100° in a vacuum is zero; the specific gravity is at its maximum; the electrical resistance begins to increase sharply at this point towards a maximum reached at approximately 100 per cent. H_2SO_4, and in connection with this the action upon iron decreases, which is of great importance for the durability of plant. Knietsch has shown also that acid of this strength absorbs sulphuric anhydride vapours very readily; a fact of which great use is made in the preparation of oleum by the contact process. Recently the thermal data obtained by Knietsch has been subjected to a critical examination by A. W. Porter,[1] and found to be unreliable, so that some doubt has been cast on the entire accuracy of his results, although his general conclusions are probably quite correct.

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[1] *Ber.*, 1901, p. 4089.

The ordinary "*rectified oil of vitriol*" usually contains more water than the acid of maximum boiling-point. Very occasionally 98 per cent. is made, but the ordinary rectified O.V. generally termed "168° Tw." varies in strength from 96 to 92

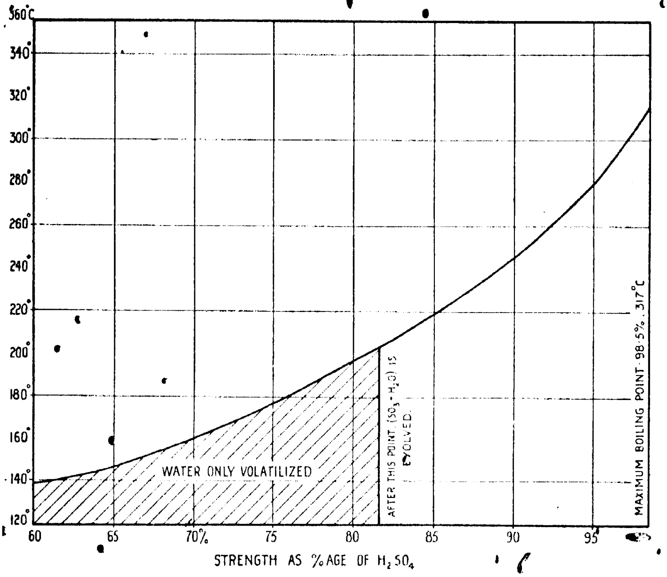

FIG. 1.—Boiling-Points of Sulphuric Acid at Various Strengths under a Barometric Pressure of 750 mm. (after Knietsch).

per cent. This variation is caused partly by the fact that at higher degrees of concentration a slight difference in specific gravity corresponds to a great difference in percentage; partly also because the specific gravity of commercial acids, owing to the presence of impurities, is always higher than that of the pure acid. It should also be observed that the correctness of ordinary hydrometers is rarely of a high order of accuracy.

The Twaddell hydrometer employed almost exclusively in

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[1] *Trans. Faraday Soc.*, 1918.

England is based on the system that 1° is equivalent to a difference in density of 0·005. On the Continent and in America, Baumé's hydrometer is used almost universally, but unfortunately the degrees of this instrument, as stated by various authorities, answer to very different specific gravities. The rational Baumé hydrometer is graduated (water = 1) according to the formula—

$$\text{Density} = \frac{144\cdot3}{144\cdot3 - n}$$

where n signifies the degree of the scale corresponding to it. This scale is adopted generally in France and Germany. In the United States, still another scale has been adopted and legalised by the Bureau of Standards (Circular No. 59.13.1916) based on the formula—

$$n \text{ (Degrees Baumé)} = 145 - \frac{145}{\text{Density}}$$

Tables of comparison of the three systems are given on page 10.

The percentage of *mixtures of sulphuric acid and water* is in the great majority of cases tested by the hydrometer only, and many tables have been constructed for this purpose, the most important being those of Lunge and Isler,[1] for strengths up to 142° Tw., and also of Lunge and Naef,[2] Pickering,[3] Worden,[4] Mendelejeff,[5] Sidersky,[6] Holler and Pfeffer.[7]

An elaborate investigation on the density of aqueous solutions of sulphuric acid has been made by Domke and Bein on behalf of the Normaleichungs Kommission at Berlin,[8] from which the tables on pages 11, 12, 13, and 14 have been prepared.

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[1] *Z. angew. Chem.*, 1890, p. 129; *J. Soc. Chem. Ind.* (*Abstr.*), 1890, p. 501.

[2] *Chem. Ind.*, 1883, p. 37.

[3] *J. Chem. Soc.*, **57**, 64 *et seq.*

[4] *J. Soc. Chem. Ind.*, 1905, pp. 178 *et seq.*

[5] *Z. physik. Chem.*, 1887, p. 273.

[6] *Ann. Chim. anal.*, 1916, p. 197; *Chem. Abstracts*, 1916, p. 320.

[7] *J. Amer. Chem. Soc.*, 1916, p. 1021; *J. Soc. Chem. Ind.* (*Abstr.*), 1916, p. 692.

[8] *Z. anorg. Chem.*, 1905, **48**, 125-181.

Comparison of Degrees Baumé with the Specific Gravities and Degrees Twaddell.

Degrees Baumé.	Rational Hydrometer.		American Hydrometer.	
	$d = \frac{144{\cdot}3}{144{\cdot}3 - n}$ (15° C.).	Corresponding Degrees Twaddell.	$d = \frac{145}{n - 145}$ (15·5° C.).	Corresponding Degrees Twaddell.
1	1·007	1·4	1·0069	1·4
2	1·014	2·8	1·0140	2·8
3	1·021	4·2	1·0211	4·2
4	1·029	5·8	1·0284	5·7
5	1·036	7·2	1·0357	7·1
6	1·043	8·6	1·0432	8·6
7	1·051	10·2	1·0507	10·1
8	1·059	11·8	1·0584	11·7
9	1·066	13·2	1·0662	13·2
10	1·074	14·8	1·0741	14·8
11	1·082	16·4	1·0821	16·4
12	1·091	18·2	1·0902	18·0
13	1·099	19·8	1·0985	19·7
14	1·107	21·4	1·1069	21·4
15	1·116	23·2	1·1154	23·1
16	1·125	25·0	1·1240	24·8
17	1·134	26·8	1·1328	26·6
18	1·143	28·6	1·1417	28·3
19	1·152	30·4	1·1508	30·2
20	1·161	32·2	1·1600	32·0
21	1·170	34·0	1·1694	33·9
22	1·180	36·0	1·1789	35·8
23	1·190	38·0	1·1885	37·7
24	1·200	40·0	1·1983	39·7
25	1·210	42·0	1·2083	41·7
26	1·220	44·0	1·2185	43·7
27	1·230	46·0	1·2288	45·8
28	1·241	48·2	1·2393	47·9
29	1·251	50·2	1·2500	50·0
30	1·262	52·4	1·2609	52·2
31	1·274	54·8	1·2719	54·4
32	1·285	57·0	1·2832	56·6
33	1·296	59·2	1·2946	58·9
34	1·308	61·6	1·3063	61·3
35	1·320	64·0	1·3182	63·6
36	1·332	66·4	1·3303	66·1
37	1·345	69·0	1·3426	68·5
38	1·357	71·4	1·3551	71·0
39	1·370	74·0	1·3679	73·6
40	1·384	76·8	1·3810	76·2
41	1·397	79·4	1·3942	78·8
42	1·411	82·2	1·4078	81·6
43	1·424	84·8	1·4216	84·3
44	1·439	87·8	1·4356	87·1
45	1·453	90·6	1·4500	90·0
46	1·468	93·6	1·4646	92·9
47	1·483	96·6	1·4796	95·9
48	1·498	99·6	1·4948	99·0
49	1·514	102·8	1·5104	102·1
50	1·530	106·0	1·5263	105·3
51	1·547	109·4	1·5426	108·5
52	1·563	112·6	1·5591	111·8
53	1·580	116·0	1·5761	115·2
54	1·598	119·6	1·5934	118·7
55	1·616	123·2	1·6111	122·2
56	1·634	126·8	1·6292	125·8
57	1·652	130·4	1·6477	129·5
58	1·672	134·4	1·6667	133·3
59	1·692	138·4	1·6860	137·2
60	1·712	142·4	1·7059	141·2
61	1·732	146·4	1·7262	145·2
62	1·753	150·6	1·7470	194·4
63	1·775	155·0	1·7683	153·7
64	1·797	159·4	1·7901	158·0
65	1·820	164·0	1·8125	162·5
66	1·843	168·6	1·8354	167·1

Specific Gravities of Sulphuric Acid.

Degrees Twaddell.	Specific gravity d 15°/4°.	100 parts by weight contain		Kilos H_2SO_4 per litre.	1 cubic foot of acid	
		SO_3.	H_2SO_4.		weighs lb. avoir.	contains lb. H_2SO_4.
1	1·005	0·69	0·84	0·0084	62·74	0·53
2	1·010	1·28	1·57	0·0159	63·05	0·99
3	1·015	1·89	2·31	0·0234	63·37	1·46
4	1·020	2·48	3·04	0·0310	63·68	1·94
5	1·025	3·10	3·79	0·0388	63·99	2·42
6	1·030	3·70	4·53	0·0467	64·30	2·91
7	1·035	4·31	5·27	0·0546	64·61	3·40
8	1·040	4·90	6·00	0·0624	64·93	3·90
9	1·045	5·49	6·72	0·0702	65·24	4·38
10	1·050	6·08	7·44	0·0781	65·55	4·88
11	1·055	6·66	8·15	0·0860	65·86	5·37
12	1·060	7·24	8·86	0·0939	66·18	5·86
13	1·065	7·81	9·56	0·1018	66·49	6·36
14	1·070	8·39	10·26	0·1098	66·80	6·86
15	1·075	8·96	10·96	0·1178	67·11	7·36
16	1·080	9·53	11·66	0·1259	67·42	7·86
17	1·085	10·09	12·35	0·1340	67·74	8·37
18	1·090	10·65	13·03	0·1420	68·05	8·87
19	1·095	11·21	13·71	0·1501	68·36	9·37
20	1·100	11·76	14·39	0·1583	68·67	9·88
21	1·105	12·32	15·07	0·1665	68·98	10·40
22	1·110	12·86	15·73	0·1746	69·30	10·90
23	1·115	13·40	16·40	0·1829	69·61	11·42
24	1·120	13·95	17·07	0·1912	69·92	11·93
25	1·125	14·49	17·73	0·1995	70·23	12·45
26	1·130	15·03	18·39	0·2078	70·55	12·97
27	1·135	15·56	19·04	0·2161	70·86	13·49
28	1·140	16·09	19·69	0·2245	71·17	14·01
29	1·145	16·62	20·34	0·2329	71·48	14·54
30	1·150	17·15	20·98	0·2413	71·79	15·06
31	1·155	17·67	21·62	0·2497	72·11	15·59
32	1·160	18·19	22·26	0·2582	72·42	16·12
33	1·165	18·72	22·90	0·2668	72·73	16·66
34	1·170	19·24	23·54	0·2754	73·04	17·19
35	1·175	19·75	24·17	0·2840	73·35	17·73
36	1·180	20·27	24·80	0·2926	73·67	18·27
37	1·185	20·78	25·43	0·3013	73·98	18·81
38	1·190	21·29	26·05	0·3100	74·29	19·35
39	1·195	21·81	26·68	0·3188	74·60	19·90
40	1·200	22·31	27·30	0·3278	74·92	20·45
41	1·205	22·82	27·92	0·3364	75·23	21·00
42	1·210	23·17	28·53	0·3452	75·54	21·55
43	1·215	23·82	29·15	0·3542	75·85	22·11
44	1·220	24·32	29·76	0·3631	76·16	22·67
45	1·225	24·82	30·37	0·3720	76·48	23·23
46	1·230	25·32	30·98	0·3810	76·79	23·79
47	1·235	25·81	31·58	0·3900	77·10	24·35
48	1·240	26·30	32·18	0·3990	77·41	24·91
49	1·245	26·79	32·78	0·4081	77·72	25·48
50	1·250	27·28	33·38	0·4172	78·04	26·05
51	1·255	27·77	33·98	0·4264	78·35	26·62

Specific Gravities of Sulphuric Acid—continued.

Degrees Twaddell.	Specific gravity d 15°/4°.	100 parts by weight contain		Kilos H_2SO_4 per litre.	1 cubic foot of acid	
		SO_3.	H_2SO_4.		weighs lb. avoir.	contains lb. H_2SO_4.
52	1·260	28·25	34·57	0·4356	78·66	27·19
53	1·265	28·74	35·17	0·4449	78·97	27·77
54	1·270	29·23	35·76	0·4515	79·29	28·35
55	1·275	29·71	36·35	0·4635	79·60	28·93
56	1·280	30·19	36·94	0·4728	79·91	29·52
57	1·285	30·67	37·52	0·4821	80·22	30·10
58	1·290	31·14	38·10	0·4919	80·53	30·68
59	1·295	31·61	38·68	0·5009	80·85	31·27
60	1·300	32·08	39·25	0·5102	81·16	31·85
61	1·305	32·56	39·83	0·5198	81·47	32·45
62	1·310	33·02	40·40	0·5292	81·78	33·04
63	1·315	33·48	40·97	0·5388	82·09	33·63
64	1·320	33·94	41·53	0·5482	82·41	34·22
65	1·325	34·40	42·09	0·5577	82·72	34·82
66	1·330	34·86	42·65	0·5672	83·03	35·41
67	1·335	35·31	43·20	0·5767	83·34	36·00
68	1·340	35·76	43·75	0·5862	83·66	36·60
69	1·345	36·21	44·30	0·5958	83·97	37·20
70	1·350	36·66	44·85	0·6055	84·28	37·80
71	1·355	37·10	45·39	0·6150	84·59	38·40
72	1·360	37·54	45·93	0·6246	84·90	39·00
73	1·365	37·97	46·46	0·6342	85·22	39·59
74	1·370	38·40	46·99	0·6438	85·53	40·19
75	1·375	38·84	47·52	0·6534	85·84	40·79
76	1·380	39·26	48·04	0·6629	86·15	41·39
77	1·385	39·69	48·56	0·6726	86·47	41·99
78	1·390	40·10	49·07	0·6821	86·78	42·58
79	1·395	40·53	49·59	0·6918	87·09	43·19
80	1·400	40·95	50·10	0·7014	87·40	43·79
81	1·405	41·36	50·61	0·7111	87·71	44·39
82	1·410	41·78	51·12	0·7208	88·02	45·00
83	1·415	42·89	51·62	0·7304	88·34	45·60
84	1·420	42·60	52·12	0·7401	88·65	46·20
85	1·425	43·01	52·62	0·7498	88·96	46·81
86	1·430	43·41	53·11	0·7595	89·27	47·41
87	1·435	43·81	53·60	0·7692	89·59	48·02
88	1·440	44·21	54·09	0·7789	89·90	48·63
89	1·445	44·61	54·58	0·7887	90·21	49·24
90	1·450	45·00	55·06	0·7984	90·52	49·84
91	1·455	45·39	55·54	0·8081	90·84	50·45
92	1·460	45·79	56·02	0·8179	91·15	51·06
93	1·465	46·18	56·50	0·8277	91·46	51·67
94	1·470	46·56	56·97	0·8375	91·77	52·28
95	1·475	46·95	57·44	0·8472	92·08	52·89
96	1·480	47·33	57·91	0·8571	92·40	53·51
97	1·485	47·71	58·38	0·8669	92·71	54·12
98	1·490	48·10	58·85	0·8769	93·02	54·74
99	1·495	48·48	59·32	0·8868	93·33	55·36
100	1·500	48·86	59·78	0·8967	93·64	55·98
101	1·505	49·23	60·24	0·9066	93·96	56·60
102	1·510	49·61	60·70	0·9166	94·27	57·22

Specific Gravities of Sulphuric Acid—continued.

Degrees Twaddell.	Specific gravity d 15°/4°.	100 parts by weight contain		Kilos H_2SO_4 per litre.	1 cubic foot of acid	
		SO_3.	H_2SO_4.		weighs lb. avoir.	contains lb. H_2SO_4.
103	1·515	49·99	61·16	0·9266	94·58	57·85
104	1·520	50·35	61·61	0·9365	94·89	58·46
105	1·525	50·73	62·07	0·9466	95·21	59·09
106	1·530	51·10	62·52	0·9566	95·52	59·72
107	1·535	51·47	62·97	0·9666	95·83	60·34
108	1·540	51·83	63·42	0·9767	96·14	60·97
109	1·545	52·20	63·87	0·9868	96·45	61·60
110	1·550	52·56	64·31	0·9968	96·77	62·23
111	1·555	52·92	64·75	1·0069	97·08	62·86
112	1·560	53·28	65·19	1·0170	97·39	63·49
113	1·565	53·64	65·63	1·0271	97·70	64·12
114	1·570	54·01	66·08	1·0375	98·01	64·77
115	1·575	54·37	66·52	1·0477	98·33	65·41
116	1·580	54·73	66·96	1·0580	98·64	66·05
117	1·585	55·09	67·40	1·0683	98·95	66·69
118	1·590	55·44	67·83	1·0785	99·26	67·33
119	1·595	55·79	68·26	1·0887	99·58	67·97
120	1·600	56·14	68·69	1·0990	99·89	68·61
121	1·605	56·49	69·12	1·1094	100·20	69·26
122	1·610	56·84	69·55	1·1198	100·51	69·91
123	1·615	57·19	69·98	1·1302	100·82	70·56
124	1·620	57·46	70·41	1·1406	101·14	71·21
125	1·625	57·89	70·83	1·1510	101·45	71·86
126	1·630	58·25	71·27	1·1617	101·76	72·52
127	1·635	58·60	71·70	1·1723	102·07	73·19
128	1·640	58·95	72·13	1·1829	102·38	73·85
129	1·645	59·30	72·55	1·1934	102·70	74·51
130	1·650	59·64	72·97	1·2040	103·01	75·17
131	1·655	59·99	73·40	1·2148	103·32	75·84
132	1·660	60·33	73·82	1·2254	103·63	76·50
133	1·665	60·68	74·24	1·2361	103·95	77·17
134	1·670	61·02	74·66	1·2468	104·26	77·84
135	1·675	61·37	75·09	1·2578	104·57	78·52
136	1·680	61·71	75·51	1·2686	104·88	79·20
137	1·685	62·06	75·93	1·2794	105·19	79·87
138	1·690	62·41	76·36	1·2905	105·51	80·56
139	1·695	62·75	76·78	1·3014	105·82	81·25
140	1·700	63·10	77·21	1·3126	106·13	81·94
141	1·705	63·45	77·63	1·3236	106·44	82·63
142	1·710	63·80	78·06	1·3348	106·75	83·33
143	1·715	64·15	78·49	1·3461	107·07	84·04
144	1·720	64·50	78·92	1·3574	107·38	84·74
145	1·725	64·85	79·35	1·3688	107·69	85·45
146	1·730	65·21	79·79	1·3804	108·00	86·18
147	1·735	65·57	80·23	1·3920	108·32	86·90
148	1·740	65·94	80·68	1·4038	108·63	87·64
149	1·745	66·31	81·14	1·4159	108·94	88·39
150	1·750	66·69	81·60	1·4280	109·25	89·15
151	1·755	67·08	82·07	1·4403	109·56	89·92
152	1·760	67·46	82·54	1·4527	109·88	90·69
153	1·765	67·85	83·02	1·4653	110·19	91·48

Specific Gravities of Sulphuric Acid—continued.

Degrees Twaddell.	Specific gravity d 15°/4°.	100 parts by weight contain		Kilos H_2SO_4 per litre.	1 cubic foot of acid	
		SO_3.	H_2SO_4.		weighs lb. avoir.	contains lb. H_2SO_4.
154	1·770	68·24	83·50	1·4779	110·50	92·27
155	1·775	68·68	84·03	1·4915	110·81	93·12
156	1·780	69·11	84·56	1·5052	111·12	93·97
157	1·785	69·57	85·12	1·5194	111·44	94·86
158	1·790	70·03	85·69	1·5338	111·75	95·76
159	1·795	70·53	86·30	1·5491	112·06	96·71
160	1·800	71·04	86·92	1·5646	112·37	97·67
161	1·805	71·60	87·61	1·5814	112·69	98·72
162	1·810	72·21	88·35	1·5991	113·00	99·83
163	1·815	72·87	89·16	1·6182	113·310	101·03
164	1·820	73·59	90·04	1·6387	113·62	102·31

Specific Gravities of Solutions containing above 90 *per cent. of Sulphuric Acid.*

Per cent. H_2SO_4	91	92	93	94	95
Density d 15°/4°	1·8248	1·8293	1·8331	1·8367	1·8388
Per cent. H_2SO_4	96	97	98	99	100
Density d 15°/4°	1·8406	1·8466	1·8411	1·8393	1·8357

A correction for any deviation of the temperature from 15° must be made whenever the acid tested by the hydrometer is above or below that temperature. The following figures are taken from a table in Lunge's *Technical Chemists' Handbook* (1913). Mean figures only are given below; for each degree above or below 15° add or subtract from the specific gravity observed.

With acids up to 1·170		(34° Tw.)	– 0·0006.
"	from 1·130 to 1·450	(34 to 90°)	– 0·0007.
"	" 1·450 " 1·580	(90 " 116°)	– 0·0008.
"	" 1·580 " 1·750	(116 " 150°)	– 0·0009.
"	" 1·750 " 1·840	(150 " 169°)	– 0·0010.

The subjoined tables have been approved and adopted as standard (23rd June 1904), by the Manufacturing Chemists Association of the United States.

The chemists responsible for the work were W. C. Ferguson and H. P. Talbot. The freezing-points assigned were calculated from Pickering's results.[1]

Specific gravity determinations were made at 60° F., compared with water at 60° F. From the specific gravities, the corresponding degrees Baumé were calculated by the following formula—

$$\text{Baumé} = 145 - \frac{145}{\text{sp. gr.}}$$

Baumé hydrometers for use with this table must be graduated by the preceding formula, which formula should always be printed on the scale.

66° Baumé = sp. gr. 1·8354. One cubic foot of water at 60° F. weighs 62·37 lb. avoirdupois. Atomic weights from F. W. Clark's table of 1901, standard—

$$O = 16. \quad H_2SO_4 = 100 \text{ per cent.}$$

	H_2SO_4	O.V.	60° Bé.
O.V. . . .	93·16	100·00	119·08
60° . . .	77·67	83·35	100·00
50° . . .	62·18	66·72	80·06

Acids stronger than 60° Bé. should have their percentage compositions determined by chemical analysis.

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[1] *J. Chem. Soc.*, 67, 363.

Bé.°	Sp. Gr.	Tw.°	Per cent. H_2SO_4.	Weight 1 cu. ft. in lbs. Av.	Per cent. O.V.	Pounds O.V. in 1 cu. ft.	Freezing (Melting) Point.
0	1·0000	0·0	0·00	62·37	0·00	0·00	32·0° F.
1	1·0069	1·4	1·02	62·80	1·05	0·68	31·2 „
2	1·0140	2·8	2·08	63·24	2·23	1·41	30·5 „
3	1·0211	4·2	3·13	63·69	3·36	2·14	29·8 „
4	1·0284	5·7	4·21	64·14	4·52	2·90	28·9 „
5	1·0357	7·1	5·28	64·60	5·67	3·66	28·1 „
6	1·0432	8·6	6·37	65·06	6·84	4·45	27·2 „
7	1·0507	10·1	7·45	65·53	7·99	5·24	26·3 „
8	1·0584	11·7	8·55	66·01	9·17	6·06	25·1 „
9	1·0662	13·2	9·66	66·50	10·37	6·89	24·0 „
10	1·0741	14·8	10·77	66·99	11·56	7·74	22·8 „
11	1·0821	16·4	11·89	67·49	12·76	8·61	21·5 „
12	1·0902	18·0	13·01	68·00	13·96	9·49	20·0 „
13	1·0985	19·7	14·13	68·51	15·16	10·39	18·3 „
14	1·1069	21·4	15·25	69·04	16·36	11·30	16·6 „
15	1·1154	23·1	16·38	69·57	17·58	12·23	14·7 „
16	1·1240	24·8	17·53	70·10	18·81	13·19	12·6 „
17	1·1328	26·6	18·71	70·65	20·08	14·18	10·2 „
18	1·1417	28·3	19·89	71·21	21·34	15·20	7·7 „
19	1·1508	30·2	21·07	71·78	22·61	16·23	4·8 „
20	1·1600	32·0	22·25	72·35	23·87	17·27	+ 1·6 „
21	1·1694	33·9	23·43	72·94	25·14	18·34	− 1·8 „
22	1·1789	35·8	24·61	73·53	26·41	19·42	− 6·0 „
23	1·1885	37·7	25·81	74·13	27·69	20·53	− 11 „
24	1·1983	39·7	27·03	74·74	29·00	21·68	− 16 „
25	1·2083	41·7	28·28	75·36	30·34	22·87	− 23 „
26	1·2185	43·7	29·53	76·00	31·69	24·08	− 30 „
27	1·2288	45·8	30·79	76·64	33·04	25·32	− 39 „
28	1·2393	47·9	32·05	77·30	34·39	26·58	− 49 „
29	1·2500	50·0	33·33	77·96	35·76	27·88	− 61 „
30	1·2609	52·2	34·63	78·64	37·16	29·22	− 73 „
31	1·2719	54·4	35·93	79·33	38·55	30·58	− 82 „
32	1·2832	56·6	37·26	80·03	39·98	32·00	− 96 „
33	1·2946	58·9	38·58	80·74	41·40	33·42	− 97 „
34	1·3063	61·3	39·92	81·47	42·83	34·90	− 91 „
35	1·3182	63·6	41·27	82·22	44·28	36·41	− 81 „
36	1·3303	66·1	42·63	82·97	45·74	37·95	− 70 „
37	1·3426	68·5	43·99	83·74	47·20	39·53	− 60 „
38	1·3551	71·0	45·35	84·52	48·66	41·13	− 53 „
39	1·3679	73·6	46·72	85·32	50·13	42·77	− 47 „
40	1·3810	76·2	48·10	86·13	51·61	44·45	− 41 „
41	1·3942	78·8	49·47	86·96	53·08	46·16	− 35 „
42	1·4078	81·6	50·87	87·80	54·58	47·92	− 31 „
43	1·4216	84·3	52·26	88·67	56·07	49·72	− 27 „
44	1·4356	87·1	53·66	89·54	57·58	51·46	− 23 „
45	1·4500	90·0	55·07	90·44	59·09	53·44	− 20 „
46	1·4646	92·9	56·48	91·35	60·60	55·36	− 14 „
47	1·4796	95·9	57·90	92·28	62·13	57·33	− 15 „
48	1·4948	99·0	59·32	93·23	63·65	59·34	− 18 „
49	1·5104	102·1	60·75	94·20	65·18	61·40	− 22 „
50	1·5263	105·3	62·18	95·20	66·72	63·52	− 27 „
51	1·5426	108·5	63·66	96·21	68·31	65·72	− 33 „
52	1·5591	111·8	65·13	97·24	69·89	67·96	− 39 „

Bé.°	Sp. Gr.	Tw.°	Per cent. H_2SO_4.	Weight 1 cu. ft. in lbs. Av.	Per cent. O.V.	Pounds O.V. in 1 cu. ft.	Freezing (Melting) Point.
53	1·5761	115·2	66·63	98·30	71·50	70·28	− 49° F.
54	1·5934	118·7	68·13	99·38	73·11	72·66	59 ,,
55	1·6111	122·2	69·65	100·48	74·74	75·10	* ,,
56	1·6292	125·8	71·17	101·61	76·37	77·60	* ,,
57	1·6477	129·5	72·75	102·77	78·07	80·23	* ,,
58	1·6667	133·3	74·36	103·95	79·79	82·95	* ,,
59	1·6860	137·2	75·99	105·16	81·54	85·75	− 7 ,,
60	1·7059	141·2	77·67	106·40	83·35	88·68	+ 12·6 ,,
61	1·7262	145·2	79·43	107·66	85·23	91·76	27·3 ,,
62	1·7470	149·4	81·30	108·96	87·24	95·06	39·1 ,,
63	1·7683	153·7	83·34	110·29	89·43	98·63	46·1 ,,
64	1·7901	158·0	85·66	111·65	91·92	102·63	46·4 ,,
64¼	1·7957	159·1	86·33	112·00	92·64	103·75	43·6 ,,
64½	1·8012	160·2	87·04	112·34	93·40	104·93	41·1 ,,
64¾	1·8068	161·4	87·81	112·69	94·23	106·19	37·9 ,,
65	1·8125	162·5	88·65	113·05	95·13	107·54	33·1 ,,
65¼	1·8182	163·6	89·55	113·40	96·10	108·97	24·6 ,,
65½	1·8239	164·8	90·60	113·76	97·22	110·60	13·4 ,,
65¾	1·8297	165·9	91·80	114·12	98·51	112·42	− 1 ,,
66	1·8354	167·1	93·19	114·47	100·00	114·47	− 29 ,,

* Below − 40.

ALLOWANCE FOR TEMPERATURE.

At 10° Bé. 0·029° Bé. or 0·00023 sp. gr. = 1° F.
,, 20° ,, 0·036° ,, 0·00034 ,, = 1° ,,
,, 30° ,, 0·035° ,, 0·00039 ,, = 1° ,,
,, 40° ,, 0·031° ,, 0·00041 ,, = 1° ,,
,, 50° ,, 0·028° ,, 0·00045 ,, = 1° ,,
,, 60° ,, 0·026° ,, 0·00053 ,, = 1° ,,
,, 63° ,, 0·026° ,, 0·00057 ,, = 1° ,,
,, 66° ,, 0·0235° ,, 0·00054 ,, = 1° ,,

APPROXIMATE BOILING-POINTS.

50° Bé. 295° F.
60° ,, 386° ,,
61° ,, 400° ,,
62° ,, 415° ,,
63° ,, 432° ,,
64° ,, 451° ,,
65° ,, 485° ,,
66° ,, 538° ,,

Influence of Impurities on the Density of Aqueous Sulphuric Acid.

The specific gravities given in all tables refer only to *pure* acid, and cannot be accepted as quite correct for the ordinary acid of trade, which always contains impurities.

The effect of the presence of arsenic trioxide has been examined by R. Kisling.[1] The specific gravities of two commercial acids, A and B, were observed at 15° C., and calculated for water at 4° C. and the vacuum, in order to be comparable with Lunge's and Naef's figures for pure acid.

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[1] *Chem. Ind.*, 1886, p. 137.

A.			B.			Pure Acid (Lunge and Naef).	
Sp. Gr. at 15°.	H_2SO_4 per cent.	As_2O_3 per cent.	Sp. Gr. at 15°.	H_2SO_4 per cent.	As_2O_3 per cent.	Sp. Gr. at $\frac{15}{4}$ in the vacuum.	H_2SO_4 per cent.
1·8377	...	0·137	1·8367	93·82	0·024	1·833	92·75
1·8387	...	0·137	1·8372	93·67	0·035	1·834	93·05
1·8393	92·87	0·192	1·8373	93·12	0·028	1·835	93·43
1·8409	93·28	0·258	1·8384	93·72	0·037	1·836	93·80
1·8412	94·25	0·219	1·8386	93·96	0·037	1·837	94·20
1·8413	93·60	0·254	1·8388	94·04	0·039	1·838	94·60
1·8414	93·93	0·231	...	...	...	1·839	95·00
1·8415	93·77	0·231	...	...	...	1·840	95·60

The effect of the presence of sulphur dioxide has been examined by J. Dunn.[1] By passing a current of pure dry SO_2 through sulphuric acid of sp. gr. 1·841, he found that this acid dissolves the amounts shown in the following table.

Temperature 0°.	Volume at N.T.P. Vols. SO_2.	Specific Gravity of Solution at Temperature of Experiment.
At 11·1	33·78	1·823
„ 16·1	28·86	...
„ 17·1	28·14	...
„ 26·9	19·27	1·822
„ 42·0	12·82	1·821
„ 50·9	9·47	1·818
„ 62·3	7·21	1·816
„ 84·2	4·54	1·809

Sulphurous acid certainly never occurs in such quantities (up to saturation) in commercial vitriol; and it is very rarely that more than traces of it are found therein, since it cannot co-exist with the nitrogen oxides which are found frequently in weak commercial vitriol. Nitrous acid has a very marked effect on the apparent percentage of a sulphuric acid as tested by the hydrometer, but is present usually in very small quantities in concentrated acid, and only in "nitrous vitriol" do such large proportions of nitrous acid occur as to influence appreciably the specific gravity of the sulphuric acid.

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[1] *Chem. News*, 1881, **43**, 121; 1882, **45**, 270.

A. Marshall[1] has made a careful study of the effect of the presence of impurities on the density of sulphuric acid. The acid recovered from the waste acid of nitrating processes may contain notable quantities of nitric acid, which make the specific gravity of the strong sulphuric acid appear higher than normal. Mixtures of both acids up to 7·5 per cent. HNO_3, show an increase of sp. gr. up to 1·862; from that onwards the specific gravities decrease. Experiments show that an additional 0·1 per cent. of various sulphates raises the specific gravity of strong sulphuric acid by 0·001; lead sulphate by 0·0015; As_2O_3 by 0·0013; nitro-sulphuric acid by 0·00027. Lead sulphate is slightly soluble in strong acid; 94 per cent. may contain 0·06 per cent. $PbSO_4$, and 98 per cent. acid up to 0·09 per cent. $PbSO_4$.

Freezing- and Melting-points.—The freezing- and melting-points of sulphuric acid of different degrees of concentration have been determined by Lunge.[2]

Spec. Grav. of Acid at 15°.	Freezing-point.	Melting-point.	Spec. Grav. of Acid at 15°.	Freezing-point.	Melting-point.
1·671	liquid at − 20°	liquid	1·767	+ 1·6	+ 6·5
1·691	do.	do.	1·790	+ 4·5	+ 8·0
1·712	do.	do.	1·807	− 9·0	− 6·8
1·727	− 7·5	− 7·5	1·822	liquid at − 20°	liquid
1·732	− 8·5	− 8·5	1·840	do.	do.
1·749	− 0·2	+ 4·5			

Further determinations have been made by Pickering,[3] Thilo,[4] Pictet,[5] and, more recently, by Girau.[6]

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[1] *J. Soc. Chem. Ind.*, 1902, p. 1508.

[2] *Ber.*, 1881, p. 2649; *J. Chem. Soc. Abstr.*, 1882, p. 149.

[3] *J. Chem. Soc.*, 1890, p. 331.

[4] *Chem. Zeit.*, 1892, p. 1688; *J. Soc. Chem. Ind.* (*Abstr.*), 1893, p. 827.

[5] *Comptes rend.*, 1894, p. 642; *J. Soc. Chem. Ind.* (*Abstr.*), 1895, p. 35.

[6] *Bull. Soc. chim.*, 1913, p. 1049; *J. Soc. Chem. Ind.* (*Abstr.*), 1913, p. 788.

Knietsch[1] gives the following table of the melting-points of sulphuric acid from 1 per cent. to 100 per cent. SO_3, which has been supplemented by adding the corresponding percentages of H_2SO_4. He takes as melting-point the temperature at which the cooled acid in which crystals had commenced to form remained constant when the vessel was taken out of the cooling medium during the process of solidification.

SO_3 per cent.	H_2SO_4 per cent.	Melting-point.	SO_3 per cent.	H_2SO_4 per cent.	Melting-point.	SO_3 per cent.	Melting-point.
		Degrees.			Degrees.		Degrees.
1	1·22	− 0·6	...	... }	below − 40	82	+ 8·2
2	2·45	− 1·0	...	... }		83	− 0·8
3	3·67	− 1·7	61	74·72	− 40	84	− 9·2
4	4·90	− 2·0	62	75·95	− 20	85	− 11·0
5	6·12	− 2·7	63	77·17	− 11·5	86	− 2·2
6	7·35	− 3·6	64	78·40	− 4·8	87	+ 13·5
7	8·57	− 4·4	65	79·62	− 4·2	88	+ 26·0
8	9·80	− 5·3	66	80·85	+ 1·2	89	+ 34·2
9	11·02	− 6·0	67	82·07	+ 8·0	90	+ 34·2
10	12·25	− 6·7	68	83·39	+ 8·0	91	+ 25·8
11	13·47	− 7·2	69	84·52	+ 7·0	92	+ 14·2
12	14·70	− 7·9	70	85·75	+ 4·0	93	+ 0·8
13	15·92	− 8·2	71	86·97	− 1·0	94	+ 4·5
14	17·15	− 9·0	72	88·20	− 7·2	95	+ 14·8
15	18·37	− 9·3	73	89·42	− 16·2	96	+ 20·3
16	19·60	− 9·8	74	90·65	− 25·0	97	+ 29·2
17	20·82	− 11·4	75	91·87	− 34·0	98	+ 33·8
18	22·05	− 13·2	76	93·10 }	− 32·0	99	+ 36·0
19	23·27	− 15·2	77	94·83 } 66° B.	− 28·2	100	+ 40·0
20	24·50	− 17·1	78	95·05 }	− 16·5	...	...
21	25·72	− 22·5	79	96·77	− 5·2	...	...
22	26·95	− 31·0	80	98·00	+ 3·0	...	...
23	28·17	− 40·1	81	99·25	+ 7·0	...	...
...	...	...	81·63	100·00	+ 10·0	...	...

Boiling-points.—The boiling-point of sulphuric monohydrate is stated by Marignac to be 338°. According to the determinations of Lunge,[2] the boiling-points of mixtures of sulphuric acid and water are as shown in Tables I. and II. on the following page.

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[1] *Ber.*, 1901, p. 4100; *J. Soc. Chem. Ind.* (*Abstr.*), 1902, pp. 172, 343.

[2] *Ber.*, 1878, p. 370.

TABLE I.

Specific Gravity.	Temperature.	Specific Gravity reduced to 15°.	Percentage of H_2SO_4.	Boiling-point.	Barometer reduced to 0° mm.
	Degrees.			Degrees.	
1·8380	17	1·8400	95·3	297	718·8
1·8325	16·5	1·8334	92·8	280	723·9
1·8240	15·5	1·8242	90·4	264	720·6
1·8130	16	1·8140	88·7	257	726·0
1·7985	15·5	1·7990	86·6	241·5	720·1
1·7800	15	1·7800	84·3	228	720·5
1·7545	16	1·7554	81·8	218	726·0
1·7400	15	1·7400	80·6	209	720·6
1·7185	17	1·7203	78·9	203·5	725·9
1·7010	18	1·7037	77·5	197	725·2
1·6750	19	1·6786	75·3	183·5	725·2
1·6590	16	1·6599	73·9	180	725·2
1·6310	17	1·6328	71·5	173	725·2
1·6055	17	1·6072	69·5	169	730·1
1·5825	15	1·5825	67·2	160	728·8
1·5600	17	1·5617	65·4	158·5	730·1
1·5420	17	1·5437	64·3	151·5	730·1
1·4935	18	1·4960	59·4	143	730·1
1·4620	17	1·4635	56·4	133	730·1
1·4000	17	1·4015	50·3	124	730·1
1·3540	17	1·3554	45·3	118·5	730·1
1·3180	17	1·3194	41·5	115	730·1
1·2620	17	1·2633	34·7	110	732·9
1·2030	17	1·2042	27·6	107	732·9
1·1120	17	1·1128	15·8	103·5	732·9
1·0575	17	1·0580	8·5	101·5	735·0

TABLE II.

(*Calculated by Graphical Interpolation.*)

Per cent. H_2SO_4.	Boiling-point.	Per cent. H_2SO_4.	Boiling-point.	Per cent. H_2SO_4.	Boiling-point.	Per cent. H_2SO_4.	Boiling-point.
	Degrees.		Degrees.		Degrees.		Degrees.
5	101	45	118·5	70	170	86	238·5
10	102	50	124	72	174·5	88	251·5
15	103·5	53	128·5	74	180·5	90	262·5
20	105	56	133	76	189	91	268
25	106·5	60	141·5	78	199	92	274·5
30	108	62·5	147	80	207	93	281·5
35	110	65	153·5	82	218·5	94	288·5
40	114	67·5	161	84	227	95	295

Vapour Pressure of Sulphuric Acid Solutions.

The vapour pressures of sulphuric acid solutions of various strengths have been determined by Regnault[1] for temperatures from 5° to 35°.

C.	H_2SO_4 + H_2O 84·5%. 1·780.	H_2SO_4 + 2 H_2O 73·1%. 1·654.	H_2SO_4 + 3 H_2O 64·5%. 1·554.	H_2SO_4 + 4 H_2O 57·6%. 1·477.	H_2SO_4 + 5 H_2O 52·1%. 1·420.	H_2SO_4 + 7 H_2O 43·7%. 1·340.	H_2SO_4 + 9 H_2O 37·7%. 1·287.	H_2SO_4 + 11 H_2O 33·1%. 1·247.	H_2SO_4 + 17 H_2O 24·3%. 1·176.
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
5	0·105	0·388	0·861	1·294	2·137	3·168	4·120	4·428	5·478
7	0·108	0·430	0·985	1·510	2·464	3·643	4·728	5·164	6·300
9	0·112	0·476	1·125	1·753	2·829	4·176	5·408	5·980	7·216
11	0·118	0·527	1·280	2·025	3·240	4·773	6·166	6·883	8·237
13	0·124	0·586	1·454	2·331	3·699	5·443	7·013	7·885	9·374
15	0·131	0·651	1·648	2·674	4·215	6·194	7·958	8·995	10·641
17	0·139	0·725	1·865	3·059	4·793	7·036	9·014	10·222	12·054
19	0·149	0·808	2·108	3·492	5·440	7·980	10·191	11·583	13·628
21	0·159	0·901	2·380	3·977	6·166	9·039	11·506	13·090	15·383
23	0·171	1·006	2·684	4·523	6·979	10·226	12·974	14·760	17·338
25	0·184	1·125	3·024	5·135	7·892	11·557	14·613	16·610	19·516
27	0·199	1·258	3·405	5·822	8·914	13·050	16·443	18·659	21·944
29	0·216	1·408	3·830	6·594	10·060	14·723	18·485	20·929	24·650
31	0·235	1·557	4·305	7·459	11·345	16·600	20·765	23·443	27·666
33	0·256	1·767	4·838	8·432	12·785	18·704	23·311	26·228	31·025
35	0·280	1·981	5·432	9·524	14·400	21·063	26·152	29·314	34·770

Determinations have also been made by Helmholtz,[2] Bronsted,[3] Dieterici,[4] and Briggs.[5]

The results of Sorel[6] and Knietsch[7] have been shown to be inaccurate by A. W. Porter,[8] who has examined the data critically with the aid of thermodynamics. The most reliable results are those of B. C. Burt,[9] who examined the vapour pressure of sulphuric acid solutions for concentrations ranging between 24·92 and 95·94 per cent. H_2SO_4, by means of a specially designed apparatus.

From the table on pp. 24-25 it will be observed that, until a high concentration and temperature are reached (say above 90 per cent. acid and 180°), the partial pressure of sulphuric acid is extremely slight, and hence the values of the total

[1] *Ann. Chim. anal.*, 1845, **3**, 179.

[2] *Wied. Ann.*, 1886, p. 532.

[3] *Z. physik. Chem.*, 1909, p. 693.

[4] *Weid. Ann.*, 1893, p. 60; 1897, p. 616.

[5] *J. Soc. Chem. Ind.*, 1903, p. 1275.

[6] *Z. angew. Chem.*, 1889, p. 272.

[7] *Ber.*, 1901, p. 4111.

[8] *Trans. Faraday Soc.*, 1918, **18**, part 3.

[9] *J. Chem. Soc.*, 1904, p. 1339.

vapour pressures recorded are due entirely to the partial pressure of aqueous vapour. This is of the utmost importance, because it is a fundamental principle in the process of concentration. When dilute solutions of sulphuric acid are evaporated, the vapour escaping consists entirely of steam, and no loss of acid occurs until a concentration of about 144° Tw. (78·92 per cent. H_2SO_4) is reached. Up to this point, therefore, the process is carried out in open lead pans (see p. 45), but, for higher concentrations, it is necessary to employ a closed system and to draw off the acid fumes evolved into a condenser. Furthermore, it affords an explanation for the well-known fact that sulphuric acid begins to lose water at comparatively low temperatures—*i.e.*, below its boiling-point, as, for example, in the cascade system of concentration, and also for the principle long recognised as sound in the working of Kessler and Gaillard plants—namely, that for large concentrating power, very large volumes of moderately hot gas, rather than a high temperature, should be aimed at.

According to Davis,[1] the temperatures at which sulphuric acid solutions lose water are as follows:—

Sulphuric	acid of	150° Tw.	begins to lose	water at	106° C.
„	„	140	„	„	80
„	„	130	„	„	65
„	„	120	„	„	50
„	„	110	„	„	46
„	„	100	„	„	37
„	„	90	„	„	26
„	„	80	„	„	19
„	„	70	„	„	17
„	„	60	„	„	16

A critical compilation of vapour pressure data has been made by R. Wilson[2] for the purpose of humidity control in laboratory work, by means of sulphuric acid solutions. The results of various observers are compared with the calculated values obtained by thermodynamical methods similar to those of Porter (see p. 29). A series of curves is given by means of which it is possible to determine readily and accurately the relative vapour pressure of any sulphuric acid solution at any

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[1] *Handbook of Chemical Engineering*, 2, 234.

[2] *J. Ind. Eng. Chem.*, 1921, p. 326.

Total Vapour Pressure of Sulphuric Acid

(Burt, *J. Chem. Soc.*,

Percentage H_2SO_4 Temperature	24·92.	30·46.	35·54.	41·01.	48·37.	54·24.	62·81.	70·78.
55° C	95·5	86·8	78·2	...	...	...	...	...
60	120·7	111·0	100·1	84·2	59·8	44·1	...	...
65	153·7	140·6	126·8	107·4	79·0	57·3	...	...
70	192·7	176·6	159·5	136·5	100·4	74·0	35·4	...
75	240·2	219·8	199·0	171·6	126·4	94·1	45·9	...
80	295·1	271·3	245·0	211·8	157·8	118·1	58·0	...
85	363·3	332·8	301·5	261·3	195·9	146·4	73·6	...
90	439·1	403·4	366·0	317·2	241·2	182·9	92·3	35·5
95	532·6	488·2	445·4	386·0	293·5	223·8	115·8	44·8
100	640·8	589·9	537·7	465·8	355·6	267·4	140·0	57·0
105	759·6 (104·8)	762·7 (107·11)	646·2	560·2	429·8	325·5	171·5	71·0
110	...	...	757·2 (109·56)	670·2	515·4	391·9	210·8	89·0
115	...	...	...	749·4 (113·21)	621·9	470·9	255·3	...
120	...	...	...	...	754·0 (120·82)	561·8	308·0	140·4
125	...	...	...	...	...	662·6	368·5	171·3
130	...	...	...	...	...	753·7 (128·7)	438·3	205·2
135	...	...	...	...	...	...	517·6	246·3
140	...	...	...	...	...	...	612·8	291·2
145	...	...	...	...	...	...	745·0 (145·85)	355·4
150	...	...	...	...	...	...	...	426·9
155	...	...	...	...	...	...	...	501·5
160	...	...	...	...	...	...	...	589·0
165	...	...	...	...	...	...	...	740·05 (166·47)
170	...	...	...	...	...	...	...	...
175	...	...	...	...	...	...	...	...
180	...	...	...	...	...	...	...	...
185	...	...	...	...	...	...	...	...
190	...	...	...	...	...	...	...	...
195	...	...	...	...	...	...	...	...
200	...	...	...	...	...	...	...	...
205	...	...	...	...	...	...	...	...
210	...	...	...	...	...	...	...	...
215	...	...	...	...	...	...	...	...
220	...	...	...	...	...	...	...	...
225	...	...	...	...	...	...	...	...
230	...	...	...	...	...	...	...	...
235	...	...	...	...	...	...	...	...

Solutions in millimetres of Mercury at 0° C.

1904, p. 1339.)

74·86.	77·26.	78·50.	81·15.	85·14.	86·61.	88·4.	91·01.	95·94.
...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...
...	...	...	...	...	..	...	...	...
...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...
...	35·1	...	...	...	...	...	...	...
...	44·8	37·7	...	...	...	...	...	...
80·8	56·1	47·7	...	...	...	...	...	...
99·5	69·3	58·2	...	...	...	...	...	...
120·4	85·5	71·8	...	...	...	...	...	...
146·9	105·1	87·4	52·8	...	...	...	...	...
178·4	127·7	108·0	65·3	31·5	...	...	...	...
221·0	156·4	133·2	82·6	39·6	...	...	...	...
260·7	188·9	163·7	101·7	51·3	37·7	...	...	...
...	229·7	196·3	124·6	63·4	...	31·8	...	...
...	273·9	235·2	150·4	77·6	57·7	38·9	...	...
...	326·6	276·8	180·9	94·1	71·2	48·5	...	...
...	387·1	329·8	218·9	115·0	87·3	59·4	...	...
...	454·3	385·7	...	137·9	105·6	72·4	...	...
...	525·7	445·8	...	164·2	126·6	87·3	45·5	...
...	610·8	520·2	...	194·1	150·4	102·3	55·6	...
...	748·3 (189·87)	597·2	...	227·9	...	120·5	67·9	...
...	...	689·6	...	269·5	...	145·2	82·2	...
...	...	756·8 (198·35)	...	307·4	...	171·5	98·1	...
...	...	...	...	361·3	...	205·3	115·9	34·1
...	...	...	...	424·6	...	...	138·2	40·8
...	...	...	...	495·2	...	...	163·2	50·1
...	...	...	...	577·8	...	...	199·3	60·8
...	...	...	...	670·3	...	...	223·6	72·2
...	...	...	...	752·9 (228·55)	...	...	263·5	85·9
...	...	...	...	...	...	...	...	106·0

temperature between 0° and 100°. In order to make possible the reproduction of these curves on a large-scale plot, a series of points is presented below.

Best Values from Vapour Pressure Curves for Sulphuric Acid Solutions.

RELATIVE VAPOUR PRESSURE VALUES AT:—

H_2SO_4.	0°.	25°.	50°.	75°.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
0	100	100	100	100
5	98·4	98·5	98·5	98·6
10	95·9	96·1	96·3	96·5
15	92·4	92·9	93·4	93·8
20	87·8	88·5	89·3	90·0
25	81·7	82·9	84·0	85·0
30	73·8	75·6	77·2	78·6
35	64·6	66·8	68·9	70·8
40	54·2	56·8	59·3	61·6
45	44·0	46·8	49·5	52·0
50	33·6	36·8	39·9	42·8
55	23·5	26·8	30·0	33·0
60	14·6	17·2	20·0	22·8
65	7·8	9·8	12·0	14·2
70	3·9	5·2	6·7	8·3
75	1·8	2·3	3·2	4·4
80	0·5	0·8	1·2	1·8

It will be noted that *relative* vapour pressures (per cent. of that of pure water at the same temperature, thus corresponding to the *relative* humidity of the air) are given rather than the absolute values in millimeters.

Specific Heat.—The specific heat of monohydrated sulphuric acid at 16° to 20° is 0·3315 (water = 1). According to Marignac, the specific heats of sulphuric-acid solutions are as follows:—

H_2SO_4 + 5 H_2O = 0·5764
„ + 10 „ = 0·7212
„ + 15 „ = 0·7919
„ + 25 „ = 0·8537
„ + 50 „ = 0·9155
„ + 100 „ = 0·9545
„ + 200 „ = 0·9747
„ + 400 „ = 0·9878.

The following table by Bode[1] is more convenient for practical use:—

Specific Gravity.	Specific Heat.	Specific Gravity.	Specific Heat.
1·842	0·3315	1·020	0·67
1·774	0·38	1·263	0·73
1·711	0·41	1·210	0·78
1·615	0·45	1·162	0·82
1·530	0·49	1·116	0·87
1·442	0·55	1·075	0·90
1·383	0·60	1·037	0·95

Other determinations have been made by Pickering[2] and Knietsch.[3]

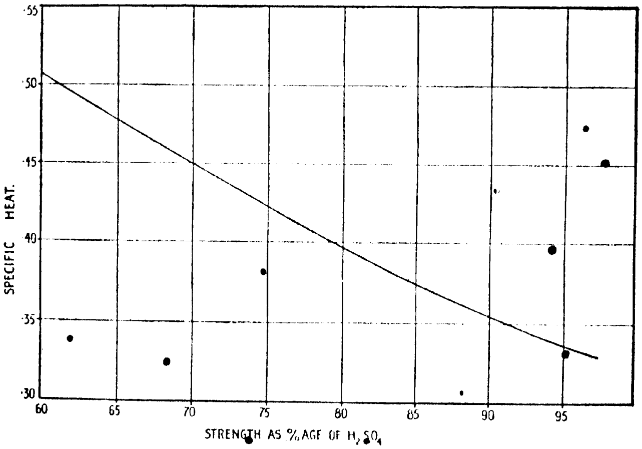

FIG. 2.—Specific Heats of Sulphuric Acid (after Bode).

The Thermal Properties of Sulphuric Acid and Water Mixtures.

When concentrated sulphuric acid is diluted with water, a considerable evolution of heat takes place, water being chemically fixed by the formation of definite hydrates. At the same time a contraction in volume occurs, which must lead equally to an evolution of heat. When concentrated acid is mixed with *snow*, excessive cold is produced by the heat becoming latent on the liquefaction of the snow, which exceeds greatly the heat set free by the chemical combination. This cold, however, is produced only when the proportion between acid and snow does not exceed certain limits: for one part of acid there must be 1¼ parts of snow present; with less snow there is a rise of temperature. Even when sulphuric acid is diluted more strongly, much heat is liberated. Thomsen[1] states that 1 gram mol. (*i.e.* 98 g.) H_2SO_4 gives the following amounts of heat when combining with x mols. of water:—

---

[1] *Z. angew. Chem.*, 1889, p. 244.
[2] *J. Chem. Soc.*, 57, 90.
[3] *Ber.*, 1901, p. 4102.

x	
1	6272 calories
2	9364 ,,
3	11108 ,,
5	13082 ,,
9	14940 ,,
19	16248 ,,
49	16676 ,,
99	16850 ,,
199	17056 ,,
499	17304 ,,
799	17632 ,,
1599	17848 ,,

These results agree well with the formula proposed by Thomsen for the heats of dilution of sulphuric acid:—

$$H' = \frac{17860 \times x}{x + 1.798}$$

in which H′ is the number of gram calories evolved when x gram mols. of water are added to 1 gram mol. of pure sulphuric acid.

According to Technical Records of Explosives Supply, No. 5, p. 121, for practical purposes it is more convenient to transform the above into an equation giving the heat H″, which is evolved when y g. of water are added to 100 g. of H_2SO_4. From the above formula H′ is the heat evolved by the addition of 18 x g. of water to 98 g. of H_2SO_4.

$$\text{Hence,} \quad H'' = \frac{100}{98} H' \text{ and } y = \frac{100}{98} \times 18x$$

$$\text{or} \quad x = \frac{98y}{1800}.$$

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[1] *Ber.*, 8, 496; *Thermochem. Untersuch.*, 8, 34.

The equation for H″ is therefore:—

$$H'' = \frac{\frac{100}{98} \times \frac{17860 \times 98y}{1800}}{\frac{98y}{1800} + 1.798}$$

$$= \frac{1786000y}{98y + 3236} \text{ calories.}$$

A more general case is that in which z g. of water are added to 100 g. of an acid consisting of x g. of water to $(100-x)$ g. of H_2SO_4. For the exact details the original paper must be consulted, but in the end the following formula is obtained:—

$$H = \frac{1000z\,(100-x)^2}{(2.029x + 100)\,(3.676x + 5.487z + 181.2)}$$

$$= \frac{1000z(100-x)^2}{Q\,(2.029x + 100)} \text{ where } Q = (3.676x + 5.487z + 181.2).$$

If the reacting qualities are given in grams, H will be expressed in gram calories, whilst if the reacting qualities are in lb., H will be in lb. Centigrade units (C.H.U.).

The most convenient type of graph for solving the equation is the "alignment chart" shown in Figs. 3 and 3*a*.

The heat of dilution of sulphuric acid has been investigated also by Pfaundler,[1] Brönsted,[2] and Knietsch.[3] The results of these observers have been examined critically by A. W. Porter[4] in a very valuable study of the thermal properties of mixtures of sulphuric acid and water. Previous data having been recorded in the neighbourhood of atmospheric temperature only, no allowance could be made for the influence of difference in temperature when the reactions took place at high temperatures (such as those obtained during the concentration of sulphuric acid). By the aid of thermodynamical reasonings, Porter has been able to supply the required information, and at the same time to check the trustworthiness of the results of previous investigators. Two different methods have been employed, and the agreement between them is within the limits of accuracy attainable in works practice. The following information has been abstracted from his paper:—

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[1] *Ber.*, 1871, p. 75; *Wien. Ber.*, 1871, p. 240.

[2] *Z. physik. Chem.*, 1906, p. 664; 1911, p. 325.

[3] *Ber.*, 1901, p. 4103.

[4] *Trans. Faraday Soc.*, 1918, part 3, pp. 373-399.

The heats of dilution of sulphuric acid with various amounts of water (heats of solution) determined by Thomsen (at 20° C.) are somewhat lower than those of Pfaundler and Brönsted (between 11° C. and 16° C.), who agree very closely together, and are to be preferred. The following are the values of the heats (in kilo calories) set free when 1 gram mol. of H_2SO_4 is diluted with n' mol. of H_2O.

n' =	0·5	1	1·5	2	4	1599
Pfaundler . .	3·67	6·776	8·68	9·998	12·858	...
Brönsted . .	3·75	6·71	8·79	10·02	12·83	19.04
Mean . .	3·71	6·74	8·73	10·01	12·84	19·04

It is more convenient, however, to specify the heat set free when 1 mol. of SO_3 is diluted with water. These numbers can be obtained by combining the above numbers with Thomsen's value for the heat of formation of H_2SO_4 from SO_3 and H_2O—namely, 21·3 kilo calories. The heat of dilution (H) of SO_3 with n mols. of H_2O is

n =	1	1·5	2	2·5	3	5	1600
H . .	21·30	25·01	28·04	30·03	31·31	34·14	40·34

These can be represented by a hyperbolic formula—

$$H = \frac{A\,n}{n+B}.$$

These values of H can be reduced so as to specify the heat set free when 1 g. of SO_3 is diluted with M g. of water. Expressing the heat in calories, the formula becomes:—

$$h_{15}\ (\text{heat of solution of } SO_3) = \frac{504.2\ M}{M+0.2013}.$$

From this formula can be calculated the true or differential heat of dilution D; that is, the heat set free when a large amount of solution containing 1 g. SO_3 to M g. H_2O is diluted with 1 g. H_2O. It is given by the differential coefficient of h with regard to M.

$$D_{15} = \frac{101.5}{(M+0.2013)^2}.$$

Values calculated from the formulæ are tabulated in Table I. and are plotted on Fig. 4.

There is a marked lack of agreement between the experimental and the graphically smoothed values of Knietsch, and the results cannot be regarded as reliable.

Latent Heat of Evaporation.—The latent heat of evaporation of the solvent of a solution can be obtained by adding the true or differential heat of dilution, D, to the latent heat of evaporation of the pure solvent.

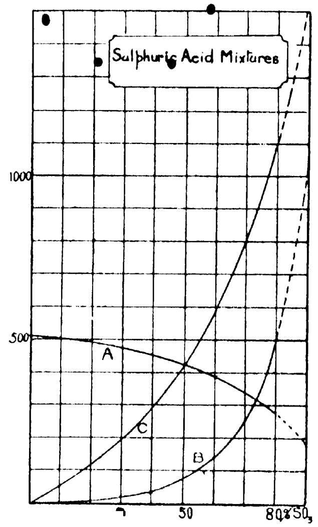

FIG. 4.—Heats of Solution and Dilution of Diluted Sulphuric Acid.

A. Heat of Solution in C.H.U.'s for amount containing 1 lb. SO$_3$.
B. Heat of Dilution per lb. water added.
C. Heat of Solution in C.H.U.'s for amount containing 1 lb. water.

$$L = L \text{ solvent} + D.$$

The values of D which are given are for the neighbourhood of 15° C.; the value of L for water at 15° C. is about 589 calories per gram. Hence, the values of L at 15° C. are:—

Per cent. SO$_3$	20	50	55	60	70	75	80
L	595	659	687	724	844	945	1088

Variation of Heats of Solution and Dilution with Temperature.—Both L water and D vary with temperature; however,

TABLE I.

Sulphuric Acid and Water.

I	Per cent. SO_3	0	20	50	55	60	70	75	80	90	100	I
	Per cent. H_2SO_4	0	24·5	61·2	67·4	73·5	85·7	91·9	98·0	Oleum	Oleum	
II	Solution contains M grams H_2O to 1 gram SO_3 : M =	Infinity	4·00	1·00	0·818	0·667	0·429	0·333	0·250	0·111	0·00	II
III	Mass of solution containing 1 gram SO_3	Infinity	5·00	2·00	1·818	1·667	1·429	1·333	1·250	1·111	1·00	III
IV	Solution contains *m* grams SO_3 to 1 gram H_2O : *m* =	0·00	0·25	1·00	1·212	1·500	2·333	3·000	4·000	9·000	Infinity	IV
V	Heat set free when 1 gram SO_3 is diluted with M grams H_2O : *h*	504·2	480	420	405	387	343	314	279	179	0	V
VI	Heat set free when SO_3 is dissolved to stated strength in 1 gram H_2O	0	120	420	495	580	800	942	1,116	1,614	2,505	VI
VII	Mass of solution containing 1 gram H_2O	1·00	1·25	2·00	2·222	2·500	3·333	4·000	5·000	10·000	Infinity	VII
VIII	Differential heat of dilution : D	0·00	5·75	70·1	97·6	135·0	255	356	499	1,040	2·505	VIII

All heat data are in calories and masses in grams, or lb.-deg. C.H.U. and pounds, and apply to 15° C.

Use of Table I.

Example I.—To find the heat set free when solution of 80 per cent. SO_3 containing 100 grams SO_3 is diluted to 60 per cent. at 15° C. :—

From V—If the 80 per cent. were diluted with infinity of water, heat set free is 100 { 504 − 279 }

If the 60 per cent. were diluted with infinity of water, heat set free is 100 { 504 − 387 }

Therefore heat required is— 100 { 387 − 279 } = **10,800** calories.

Example II.—SO_3 is dissolved in solution of 55 per cent. SO_3 strength containing 1000 grams water, and the final strength is 75 per cent. SO_3. What is the heat evolved?

From VI it is— 1000 { 942 − 495 } = **447,800** calories.

There is a marked lack of agreement between the experimental and the graphically smoothed values of Knietsch, and the results cannot be regarded as reliable.

Latent Heat of Evaporation.—The latent heat of evaporation of the solvent of a solution can be obtained by adding the true or differential heat of dilution, D, to the latent heat of evaporation of the pure solvent.

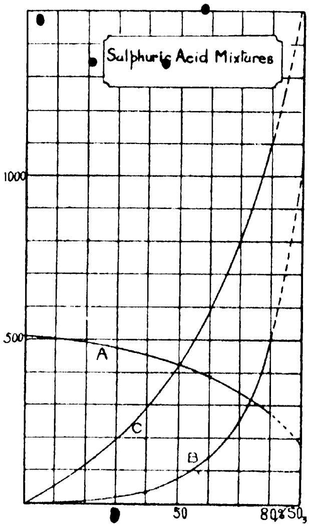

FIG. 4.—Heats of Solution and Dilution of Diluted Sulphuric Acid.

A. Heat of Solution in C.H.U.'s for amount containing 1 lb. SO$_3$.
B. Heat of Dilution per lb. water added.
C. Heat of Solution in C.H.U.'s for amount containing 1 lb. water.

$$L = L \text{ solvent} + D.$$

The values of D which are given are for the neighbourhood of 15° C.; the value of L for water at 15° C. is about 589 calories per gram. Hence, the values of L at 15° C. are:—

Per cent. SO$_3$	20	50	55	60	70	75	80
L	595	659	687	724	844	945	108·8

Variation of Heats of Solution and Dilution with Temperature.—Both L water and D vary with temperature; however.

TABLE II.

Heat of Solution at Various Temperatures.

Per cent. SO_3.	15° C.	100° C.	150° C.	200° C.
30	480	540	575	611
50	420	477	511	544
55	405	461	495	528
60	387	442	475	508
70	343	396	427	458
75	314	365	395	426
80	279	328	356	385
90	179	218	241	264

Values of h_t.

TABLE III.

Differential Heat of Dilution at Various Temperatures.

Per cent. SO_3.	15° C.	100° C.	150° C.	200° C.
20	5·75	5·97	6·11	6·25
50	70·1	73·4	75·4	77·3
55	97·6	102·4	105·3	108·1
60	135	142	146	150·3
70	255	271	280	289
75	356	380	394	408
80	499	538	560	583
90	1040	1166	1240	1314

Values of D_t.

All data in Tables II. and III. are in terms of calories and grams or lb. C.H.U. and lbs.

TABLE IV.

Latent Heat of Evaporation from Solution in Calories per Gram of Water evaporated, or in lb. Cent.-deg. H.U. per lb. of Water evaporated.

Per cent. SO_3.	15° C.	100° C.	150° C.	200° C.
20	595	545	510	467
50	659	612	579	538
55	687	641	609	569
60	724	681	650	611
70	844	810	784	750
75	945	919	898	869
80	1088	1077	1064	1044

Heat of Concentration of Acid by Evaporation (as in a Gaillard Tower).

The heat required to concentrate sulphuric acid from any one strength to any other can be divided into three main headings:—

(1) The heat required to overcome the chemical affinity between sulphuric acid and water.

(2) The heat required for the vaporisation of the water to be driven off.

(3) The amount required as "sensible" heat—*i.e.* to raise the temperature of the mixture to the point at which water is evaporated.

Porter has shown that data for the first two values can be obtained, as follows:—

Taking as standard an amount of dilute acid containing 1 g. SO_3 and M_1 g. of water, the total heat required to evaporate it at constant temperature till it contains only M_2 g. of water, is given by:—

$$\text{Heat required} = hm_1 + \text{L water}\ (M_1 - M_2) - hm_2.$$

where hm_1 represents the heat required (theoretically) to dissociate the acid completely into SO_3 and H_2O, $L\,(M_1 - M_2)$, the heat required to evaporate the given amount of water to leave M_2 g. in the finished acid, and hm_2 the heat evolved when M_2 g. of water are mixed (theoretically) with the SO_3 to yield the finished acid. The value that the above expression takes when M_2 is zero, is called by Porter "The heat of total evaporation." If this quantity is plotted for different strengths, it is only necessary to take the difference of the numbers corresponding to the two strengths at the beginning and end of the process, each at the temperature of evaporation, to obtain the heat of concentration required. A detailed set of values is given in Table V. headed "Heat of Total Evaporation."

Sensible Heat.—During the evaporation process, changes of temperature take place, so that a knowledge of the thermal

TABLE V.

Sulphuric Acid and Water Mixtures.

HEAT OF TOTAL EVAPORATION.

% SO_3.	20° C.	40°.	60°.	80°.	100°.	120°.	140°.	160°.	180°.	200°.	220°.	240°.
40	1337	1333	1330	1326	1321	1315	1307	1300	1288	1273	1257	1239
41	1294	1292	1289	1286	1283	1280	1273	1267	1251	1237	1223	1207
42	1255	1254	1252	1250	1247	1244	1238	1233	1219	1207	1194	1180
43	1218	1218	1216	1214	1212	1209	1204	1199	1187	1176	1164	1152
44	1184	1184	1182	1181	1179	1177	1173	1169	1158	1149	1138	1127
45	1151	1152	1151	1150	1148	1146	1143	1140	1131	1124	1112	1102
46	1121	1122	1122	1121	1120	1119	1117	1114	1107	1100	1087	1077
47	1090	1092	1092	1092	1092	1091	1090	1088	1083	1076	1063	1053
48	1062	1064	1064	1064	1064	1064	1064	1062	1058	1052	1040	1030
49	1035	1037	1039	1039	1039	1040	1040	1038	1034	1029	1019	1009
50	1009	1011	1014	1015	1016	1017	1017	1015	1011	1006	998	988
51	984	987	990	992	993	994	994	993	990	986	978	968
52	960	963	966	968	970	971	972	971	969	965	958	949
53	936	939	942	945	947	949	950	949	948	945	938	930
54	912	915	918	921	924	926	928	928	927	925	919	912
55	888	892	896	899	902	905	907	907	907	905	901	894
56	866	871	875	879	882	885	887	887	888	886	884	879
57	844	849	854	859	862	865	867	869	870	868	866	860
58	823	828	833	838	842	845	848	850	852	851	848	844
59	802	807	812	817	821	825	829	831	834	834	831	828
60	781	786	791	796	800	805	810	813	816	816	815	812
61	761	767	772	777	782	787	792	796	799	799	799	797
62	742	746	753	759	765	770	774	778	782	783	784	782
63	723	729	735	741	747	752	757	762	766	767	769	767
64	704	711	717	724	730	735	740	745	750	753	755	752
65	685	692	699	706	713	719	723	729	734	738	740	738
66	667	675	682	689	696	702	706	712	718	723	725	724
67	649	657	665	672	679	685	690	696	702	708	710	710
68	631	639	647	655	662	669	674	680	686	692	694	695
69	614	622	630	638	645	652	657	664	670	676	678	681
70	597	605	613	621	628	635	641	648	654	660	662	666
71	580	588	596	604	611	618	625	632	638	644	646	651
72	563	571	579	587	594	602	609	616	622	628	631	635
73	546	554	562	570	578	585	592	599	606	612	616	619
74	529	537	545	554	562	569	576	583	590	596	601	604
75	512	520	528	537	546	553	560	567	574	580	586	589
76	495	504	512	521	529	537	544	551	558	564	571	574
77	478	487	496	505	513	521	528	535	542	548	555	559
78	461	471	480	488	496	504	512	519	526	532	539	544
79	444	454	464	472	480	488	496	503	510	516	523	529
80	428	438	447	456	464	472	480	487	494	500	507	514

To find the heat required to evaporate mixture containing *m* lb. SO_3 from any one percentage to any other, at constant temperature, subtract the data in this table which relate to these percentages and temperature and multiply by *m*. The result is expressed in lb. C.H.U.'s.

capacities of sulphuric acid solutions is necessary. These, multiplied into the change of temperature, give the sensible heats required. A set of values is tabulated in Table VI. This table is also of great use for calculating the amount of cooling water required to cool down acid of any given strength from one temperature to another. The heat of total evaporation plus the sensible heat, give the total heat required in the concentration process, with an uncertainty which is measured by the variation in the amount of external work done, and which depends upon the precise method of evaporation. It is interesting and advantageous that the heat of total evaporation varies comparatively little with temperature.

Examples of the Use of the Tables.

(1) Conversion of a 55 per cent. SO_3 solution containing 1 g. SO_3 at 100° to 75 per cent. SO_3 at 200°.

(*a*) First suppose that the evaporation at constant temperature is succeeded by the temperature change. To evaporate this solution at 55 per cent. to a solution at 75 per cent. SO_3 at 100° requires (see Table V.) . 902 − 546 = 356 calories.
To raise 75 per cent. to 200° requires 101 − 51 = 50 „
Total . . 406 „

(*b*) Suppose the temperature change to occur first and to be succeeded by the evaporation. To raise original solution from 100° to 200° requires . . 187 − 93 = 94 calories.
To evaporate it at 200° requires . 905 − 580 = 325 „
Total . . 419 „

The difference between these two modes of evaporation is due to the difference in external work done. Any other mode of evaporation which does not bring the material to a higher intermediate temperature than 200° will require an intermediate amount of heat.

Considering in the same way extreme concentrations, 53 per cent. SO_3 (*i.e.* 65 per cent. H_2SO_4) and 77·7 per cent. SO_3 (*i.e.*

TABLE

Sulphuric Acid

SENSIBLE HEAT AT

% SO_3.	20° C.	40°.	60°.	80°.	100°.	120°.	140°.	160°.	180°.	200°.
40	33	66	98	131	164	197	230	262	295	328
41	32	63	95	126	158	190	221	253	284	316
42	30	61	91	122	152	182	213	243	274	304
43	29	58	88	117	146	175	204	234	263	292
44	28	56	84	112	140	168	196	224	252	280
45	27	54	81	107	134	161	188	215	242	269
46	26	52	77	103	129	155	181	207	233	258
47	25	50	75	99	124	149	174	199	224	249
48	24	48	72	96	120	144	168	191	216	239
49	23	46	69	92	115	138	161	184	207	230
50	22	44	66	89	111	133	155	177	199	222
51	21	43	64	85	107	128	149	170	192	213
52	21	41	62	82	103	124	144	165	185	206
53	20	40	60	80	100	119	139	159	179	199
54	19	39	58	77	96	116	135	154	173	193
55	19	37	56	75	93	112	131	149	168	187
56	18	36	54	72	90	108	126	144	162	181
57	17	35	53	70	88	105	123	140	158	175
58	17	34	51	68	86	102	119	136	153	170
59	16	33	49	66	82	99	115	132	148	165
60	16	32	48	64	80	96	112	128	144	160
61	15	31	46	63	77	93	108	124	139	155
62	15	30	45	60	75	90	105	120	135	150
63	14	29	44	58	73	87	102	116	131	145
64	14	28	42	56	70	85	99	113	127	141
65	14	27	41	55	68	82	96	109	123	137
66	13	27	40	53	66	80	93	106	119	133
67	13	26	39	51	64	77	90	103	116	129
68	12	25	37	50	62	75	87	100	112	125
69	12	24	36	48	60	73	85	97	109	121
70	12	23	35	47	59	70	82	94	106	117
71	11	23	34	46	57	68	80	91	102	114
72	11	22	33	44	55	66	77	88	99	110
73	11	21	32	43	54	64	75	86	97	107
74	10	21	31	42	52	62	73	83	94	104
75	10	20	30	41	51	61	71	81	91	101
76	10	20	29	39	49	59	69	79	89	98
77	9	19	29	38	48	57	67	76	86	95
78	9	18	28	37	46	56	65	74	83	93
79	9	18	27	36	45	54	63	72	81	90
80	9	17	26	34	44	52	61	70	79	87

To obtain the heat in lb. C.H.U.'s required to warm a quantity of acid of given
any other temperature, subtract the number which corresponds to the lower temperature

VI.

and Water Mixtures.

CONSTANT CONCENTRATION.

220°.	240°.	Differences: 2°.	4°.	6°.	8°.	10°.	12°.	14°.	16°.	18°.
361	394	3	7	10	13	16	20	23	26	29
348	379	3	6	9	13	16	19	22	25	28
334	365	3	6	9	12	15	18	21	24	27
321	350	3	6	9	12	15	17	20	23	26
308	336	3	6	8	11	14	17	20	22	25
296	323	3	5	8	11	13	16	19	21	24
284	310	3	5	8	10	13	15	18	21	23
274	299	2	5	7	10	12	15	17	20	22
263	287	2	5	7	10	12	14	17	19	22
253	276	2	5	7	9	11	14	16	18	21
244	266	2	4	7	9	11	13	15	18	20
234	256	2	4	6	8	11	13	15	17	19
227	247	2	4	6	8	10	12	14	16	18
219	239	2	4	6	8	10	12	14	16	18
212	231	2	4	6	8	10	12	13	15	17
205	224	2	4	6	7	9	11	13	15	17
198	217	2	4	5	7	9	11	13	14	16
193	210	2	3	5	7	9	10	12	14	16
187	204	2	3	5	7	9	10	12	14	15
181	198	2	3	5	7	8	10	11	13	15
176	192	2	3	5	6	8	10	11	13	14
170	186	1	3	5	6	8	9	11	12	14
165	180	1	3	4	6	7	9	10	12	13
160	174	1	3	4	6	7	9	10	12	13
155	169	1	3	4	6	7	8	10	11	13
150	164	1	3	4	5	7	8	10	11	12
146	159	1	3	4	5	7	8	9	11	12
142	155	1	3	4	5	6	8	9	10	12
137	149	1	2	4	5	6	7	9	10	11
133	145	1	2	4	5	6	7	8	10	11
129	141	1	2	3	5	6	7	8	9	11
125	137	1	2	3	5	6	7	8	9	10
121	133	1	2	3	4	5	7	8	9	10
118	129	1	2	3	4	5	6	7	9	10
115	125	1	2	3	4	5	6	7	8	9
111	122	1	2	3	4	5	6	7	8	9
108	118	1	2	3	4	5	6	7	8	9
105	114	1	2	3	4	5	6	7	8	9
102	111	1	2	3	4	5	6	6	7	8
99	108	1	2	3	4	4	5	6	7	8
96	105	1	2	3	3	4	5	6	7	8

percentage SO_3 in which the total quantity of SO_3 is *m* lb. from any temperature to from that which corresponds to the higher and multiply by *m*.

95 per cent. H_2SO_4), and extreme temperatures 15° and 200°, we get:—

	For 1 g. SO_3.	From Table No. V.
Evaporation at 15° C.	935 − 465	= 470 calories.
Sensible heat to raise 77·7 per cent. SO_3 from 15° C. to 200° C.		= 89 "
	Total per gram SO_3	559 "
For 100 g. 95 per cent. H_2SO_4 which contains 77·7 g. SO_3, the amount of heat is		43,400 "

	For 1 g. SO_3.	From Table No. VI.
Sensible heat to raise 53 per cent. SO_3 from 15° to 200° C		= 188 calories.
Evaporation at 200° C.	945 − 537	= 408 "
	Total	596 "
For 100 g. 95 per cent. H_2SO_4, total heat required		46,300 "

If evaporation and rise of temperature proceed concomitantly, the heat required will be intermediate to these two values.

The original paper contains detailed information of the method of construction of a simple "alignment chart," from which the values can be read off readily.

All the data are given primarily in terms of grams and calories, but the same numbers also hold if the units are kilograms and kilo calories, or pounds and pound-degree C heat units, or tons and ton-degree C heat units. If pounds and British Thermal Units (B.T.U.) are employed, the numbers require to be multiplied by $\frac{9}{5}$.

The Preparation of Anhydrous Sulphuric Acid

(100 per cent. H_2SO_4).

For some purposes sulphuric acid containing no water, or hardly any, and corresponding as nearly as possible to the formula H_2SO_4 (81·63 per cent. SO_3 and 18·37 per cent. H_2O) is required. Such acid is extremely useful in certain nitrating and sulphonating operations, connected with the manufacture of explosives and of dyes. Prior to the development of the contact system for the production of oleum on a large scale, several methods were employed for its preparation.

Mayers (B. P. 1201 of 1878) proposed to pass burner gas through sulphuric acid, so as to dissolve the SO_3 in the latter, and bring up its strength.

A new principle was proposed by Lunge[1] (B. P. 96 of 1883), namely, to freeze out the crystals of anhydrous acid from concentrated oil of vitriol; the process was carried out on a large scale for several years in England (Widnes), France (Petit Quevilly), and Germany (Griesheim), but fell into disuse with the introduction of cheap oleum by the contact process. The method adopted by Lunge is very fully described with drawings in the fourth edition (pp. 1214-1217), which should be consulted for further information.

Osterberger and Capelle[2] describe the process as carried out at Petit Quevilly. Additional information is given by Morance.[3]

Duron (Fr. P. 430145) enriches sulphuric acid by SO_3 produced by the dissociation of a portion of the concentrated acid by means of heated air, the waste heat of which is then utilised for the concentration of the dilute acid in a "concentrator" and "regenerator"; the air is finally deprived of the last traces of acid in a condenser. Dilute acid is supplied to the regenerator, where it is concentrated by the heated gas, and part of the acid is then used in the lowest stage of a "separator" tower for absorbing water from the dissociated acid vapours; the upper part of the tower being fed with 96 to 98 per cent. sulphuric acid from the concentrator for the absorption of SO_3 from the same vapours. The concentrator receives most of the acid from the regenerator (situated above it), and is so arranged that the heated air passes rapidly in a thin layer over the surface of the acid without giving rise to agitation of the liquids.

The modern process consists in absorbing sulphuric anhydride obtained by the contact process, in highly concentrated sulphuric acid.

Weber[4] (U.S. P. 1233626 of 1917; 1291306 of 1919) absorbs sulphuric anhydride in cooled and stirred 100 per cent. sulphuric acid, until at least 5 per cent. of the anhydride is absorbed; dilute sulphuric acid is then added, until the acid is of the desired strength—*i.e.* 98 per cent. In this way, the difficulties of absorbing sulphur trioxide in weak acid are avoided, and iron vessels may be used without any danger of the acid acting on the metal.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1883, p. 414; B. P. 4430 of 1887; *J. Soc. Chem. Ind.* (*Abstr.*), 1888, p. 209.

[2] *Bull. Soc. Ind. Rouen*, 1889, **17**, 307; *J. Soc. Chem. Ind.* (*Abstr.*), 1890, **9**, 390, 507.

[3] *Comptes rend.*, 1909, **148**, 842; *J. Soc. Chem. Ind.* (*Abstr.*), 1909, **28**, 520.

[4] *J. Soc. Chem. Ind.* (*Abstr.*), 1919, **38**, 499.

The Properties of Anhydrous Sulphuric Acid.

The proper sulphuric hydrate, commonly known as monohydrated sulphuric acid, has the rational formula—

$$SO_2{<}^{OH}_{OH}$$

and can be considered as containing 81·63 per cent. sulphuric anhydride and 18·37 per cent. water. It is a limpid, colourless, oily liquid. Its specific gravity at 0° is 1·853; at 15° (compared with water of 4°) 1·8384 (Lunge and Naef), 1·8378 (Schertel), 1·8372 (Marignac, F. Kohlrausch, Mendelejeff).[1] The value is given as 1·8357 by J. Domke, who has made a very elaborate investigation on the density of sulphuric acid on behalf of the Normaleichungs Kommission at Berlin.[2] The specific gravity changes to the extent of + 0·001 for each degree Centigrade. The pure monohydrate solidifies at about 0°, and forms large plate-shaped crystals which melt at + 10°·5; they remain liquid a good deal below that temperature, but solidify on agitation, or even better when a fragment of the solid hydrate is introduced. (The Chem. Fabrik Griesheim (D.R.P. 24402) make use of this property to prepare pure monohydrate).[3] The acid begins to boil at 290°, but the boiling-point rises up to 338° (Marignac). This shows that it does not distil unchanged; in fact a mixture of hydrated acid, anhydride, and water passes over (see below). This dissociation begins much earlier; the pure monohydrate produces fumes by giving off SO_3, very slightly even at the ordinary summer temperature, distinctly at 30° or 40°. Accordingly, it cannot be obtained by boiling down or distilling dilute acid; but it can be prepared by adding an exactly sufficient quantity of anhydride to the strongest acid obtainable by concentration, or by cooling ordinary concentrated acid below 0° and repeating this process of crystallisation until the pure monohydrate is obtained.

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[1] *Ber.*, 1884, pp. 1748, 2536, 2711.

[2] *Z. anorg. Chem.*, 1905, **48**, 125-181.

[3] Compare also *Chem. Abstracts*, 1914, **8**, 3540.

The vapour of sulphuric acid consists for the most part, or even entirely (according to the temperature), not of molecules of H_2SO_4 but of SO_3 and H_2O. The theoretical vapour density for H_2SO_4 (2 vols.) is 3·386, and for the completely dissociated molecules of SO_3 and H_2O (4 vols.) 1·693. Deville and Troost at 440° found the vapour density to be 1·74, so that dissociation is almost complete in the state of vapour.[1]

Oddo and Anelli[2] found the vapour density of absolutely pure H_2SO_4 rather higher than calculated from this formula, which proves that some molecules of $(H_2SO_4)_2$ are present as well as H_2SO_4, SO_3, and H_2O. In solution they assume the sulphuric acid to be present always as the dimeric molecule $(H_2SO_4)_2$. Further detailed investigations on the properties of absolutely pure H_2SO_4 have been made by Nichty,[3] Hantzsch,[4] Armstrong and Worley.[5]

Sulphuric Acid Monohydrate (H_2SO_4, H_2O).

Donk[6] has obtained crystalline sulphuric acid monohydrate H_2SO_4, H_2O by mixing 40 parts of lead or barium sulphate with 60 parts 85 per cent. sulphuric acid, and setting the mixture away at 0° overnight. A portion of the crystallised mass thus obtained is used then for seeding or inoculating a new portion of 85 per cent. sulphuric acid, which has also been kept overnight at 0°, when the acid crystallises rapidly. The crystals are monoclinic. Crystalline H_2SO_4 is obtained similarly by seeding 99·9 per cent. sulphuric acid with a portion of a solidified mixture of 60 g. 99·9 per cent. sulphuric acid, and 40 g. of lead sulphate. Crystallised H_2SO_4 is more difficult to obtain than crystallised H_2SO_4, H_2O, and is not formed if the acid is weaker than 99·5 per cent.

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[1] Dittmar, *Chem. News*, 1869, p. 258.

[2] *Gazz. Chim. Ital.*, 1911, p. 552; *Chem. Zeit.*, 1911, p. 846.

[3] *Amer. Chem. Soc.*, 1908, pp. 1834-46.

[4] *Z. physik. Chem.*, 1907, pp. 257-312.

[5] *Roy. Soc. Proc.*, 1914, **90** A, 73; *J. Soc. Chem. Ind.* (*Abstr.*), 1914, p. 960.

[6] *Chem. Weekblad.*, 1913, p. 956; *Amer. Chem. Soc.* (*Abstr.*), 1914, **2**, 1926.

Jorissen[1] states that he prepares crystallised H_2SO_4, H_2O (85 per cent. H_2SO_4) by cooling 84·0 per cent. and 83·3 per cent. solutions in melting ice. Nearly 100 per cent. H_2SO_4 may be made to crystallise by cooling 200 c.c. fuming oil of vitriol (containing 7·5 per cent. SO_3) mixed with 50 c.c. 93 per cent. sulphuric acid in ice.

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[1] *Chem. Weekblad.*, 1913, p. 962; *Amer. Abstr.*, p. 3540.

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CHAPTER III

CONCENTRATION IN HEATED PANS OR RETORTS

Lead Pans Heated from above.

THIS is the appropriate mode of firing when the purity, and especially the appearance, of the acid are of less moment than saving fuel and the accomplishment of a large amount of work. The acid in this case is, of course, contaminated by the flue dust, and is always more or less stained by sooty matter, whence its English name "brown vitriol," has arisen. These contaminations are quite harmless when it is used for decomposing salt, for superphosphate manufacture, and for many other purposes. On the other hand, the rate of evaporation in top-heated pans is very quick, because, first, the hot gas is brought into intimate contact with the acid, and can thus communicate its heat much better than when the two are separated by metallic plates, etc.; secondly, the vapours formed thereby are removed at once by the draught, which, as is well known from experience, very much assists the evaporation. Moreover, fired from the top, the pans, if properly constructed, are much less acted upon than when fired from below; the risk that, owing to the workmen's carelessness, they may be burned through, is especially diminished.

Concerning the loss of acid in this style of evaporation, no experiments have been published; probably it is somewhat larger than with pans heated from below, as the stream of fire gases, acting upon the boiling acid, carries some of it away in the so-called "vesicular" form—*i.e.*, as a mist of minute liquid drops, which is much more difficult to condense than the vapour form.

Over-heat pans are used extensively for several purposes:—

(1) For the concentration of weak chamber acid after dearsenication (see Vol. II.) to bring it up to a strength suitable for sale as "brown oil of vitriol."

(2) For strengthening the circulating acid of a chamber plant for use on the Gay Lussac towers, where for any reason the Glover towers are not sufficiently hot to do the whole of the work required.

(3) For the re-concentration of the acid obtained in Hasenclever's modification of the Deacon process for making chlorine (B. P. 3393 of 1883). He used over-heat pans when he introduced this process, and since that time they have been associated with his name, although they were described by Lunge in the first edition of this work in 1879. In this process the gas from the saltcake pots alone is fit to use directly in the decomposers. The acid evolved from the roasters is condensed in water in the usual way, and then regasified by running it into jars, through which hot vitriol circulates at about 144° to 145° Tw.—air being blown in at the same time. In this way the hydrochloric acid is evolved in a gaseous form of a strength and purity suitable for the Deacon process, whilst the water in which it was condensed previously is retained in the sulphuric acid, and has to be removed by taking the acid, which leaves the jars at about 120° Tw., and reconcentrating in an over-heat pan.

Pans heated from above have been described by Godin[1] and Lunge,[2] and many modifications have been used, but in any case the lead must be protected from direct contact with the fire, or at least the pan must be cooled in such a manner that the lead cannot melt. The best way of doing this is to keep the pan always filled to the same level, nearly to its top, leaving only a sufficient margin to prevent any from boiling over. In ordinary work the acid is never drawn off, except for repairs; but the concentrated acid is heavier and sinks down; it is continually drawn off from the bottom, and fresh acid is run constantly in at the top, as long as the concentrating process goes on. Even then the empty portion of the pan must be protected, especially at the fire-bridge. A detailed description, with drawings of the pans formerly employed, is given in the fourth edition of this work (pp. 1082-1086); but this has been omitted from the present edition, as these pans have been superseded by more modern plants.

The author is indebted to the courtesy of the United Alkali

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[1] *Annales des Mines*, 1865, p. 344. [2] *Dingl. polyt. J.*, 1871, pp. 201, 352.

Company, Ltd., Liverpool, for a description of a modern over-heat pan.

As shown in Fig. 5, the modern pan is built on a much larger scale than formerly, and measures 50 ft. long by 10 ft. wide by 2 ft. 2 in. deep inside (lead measure); the lead used weighs 20 lb. to the square foot. The leadwork is protected inside with walls of 9 in. brickwork, with the exception of 12 ft. from the furnace end, where, on account of the extra heat, the lining is 14 in. brickwork, with a half-inch cavity lined with a packing of oakum, red lead, and boiled linseed oil well mixed together. The bottom is protected with a 3-in. layer of loose bricks. The depth of brickwork from the crown of the arch is 4 ft. 9 in. at the furnace end, and tapers down for the first 13 ft. to 2 ft. 11 in., at which depth it continues to the smoke outlet. The arch is 9 in. thick, with 9 in. camber. Metalline bricks are used throughout, and all brickwork is set with sulphate of lead and boiled oil. In this way the repair costs have been reduced appreciably. There are four cleaning holes on the top of the arch, 18 in. diameter, with loose circular covers. The leadwork is carried on small steel girders, 4 in. by 2 in., in section, and about 3-in. centres resting on three larger 12-in. by 6-in. girders elevated upon eight columns to the height required for the flow of liquor. The sides are supported with cast-iron interchangeable grids, 5 ft. by 1 ft. 10 in. by 1¼ in.; and any grid can be released for repairs to leadwork. The buck stays, which are 3½ in. by 2½ in., are carried sufficiently high over the arch of the pan, and below the main girders, and connected together across the pan with 1¼-in. wrought-iron tie-rods. On each side of the buck stays are pieces of iron, 2½ in. by 1¼ in. secured with bolts, which hold the interchangeable grids in position.

The fire-stack is built 3 ft. clear from the end of the pan, and is built of 18 in. brickwork, the inner 9 in. lining being fire-brick. The furnace is 5 ft. by 3 ft. 3 in. inside; and there are two separate furnace doors for firing purposes. The smoke-stack outlet at the opposite end is 18 in. square inside brickwork. Double fires are an advantage, as they allow alternate working, so that one fire can be cleaned or charged when the other is burning brightly; thus consuming the smoke and reducing contamination and discoloration of the acid in the pan. In

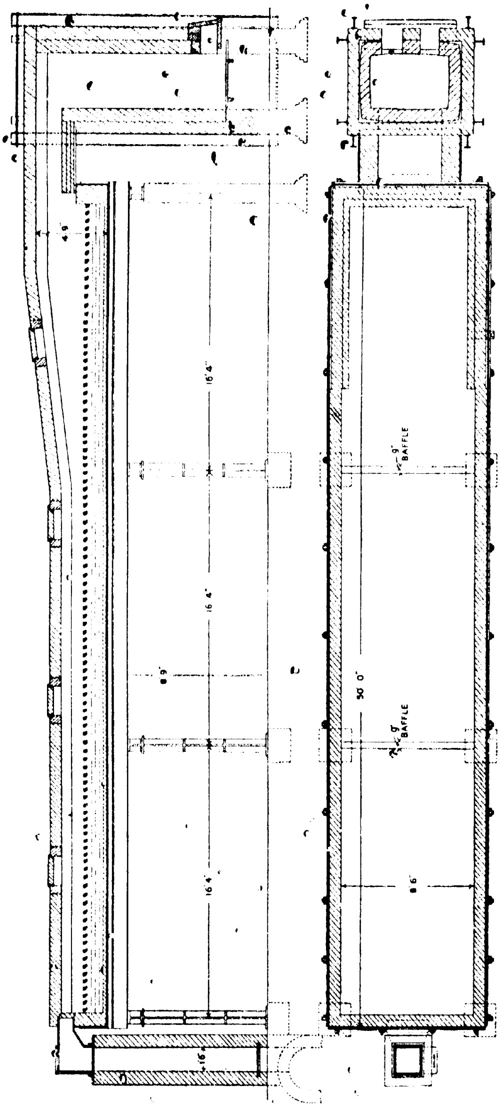

FIG. 5.

practice a fresh supply of fuel is added every one and a half to two hours, on alternate fires, and clinkering is done every eight to twelve hours, according to the quality of the fuel. It is absolutely necessary for the gas exit stack to be kept clean, as, otherwise, the furnace and neck to the pan suffer considerably.

The weak vitriol is fed into the pan at the cool end, and passes out at the end nearest the furnace—the pipes being luted below the acid level. When concentrating clean acid a pan runs for two to three years without cleaning; the necessity, for which is shown by the SO_3 test in the exit gases, rising from the normal 1 to 1·5 gr. per cubic foot when the pan is cleaned, to well over 4 gr. per cubic foot when dirty.

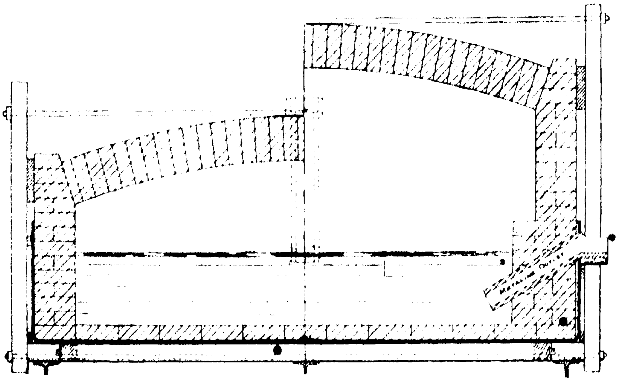

FIG. 6.

The pan constructed as in Figs. 5 and 6 is capable of producing at least 250 tons of 140° Tw. acid per week from a feed of 105° Tw., and the water evaporated is about 3 lb. for each lb. of fuel used. The loss in evaporation is about 2½ per cent.

Efforts have been made to increase the efficiency of overheat pans, by introducing two or three baffles built up to the arch, as shown in Fig. 7. These lead to a considerable improvement in efficiency; for example, during a measured run over four and a half months, the water evaporated per lb. of fuel averaged 3·76 lb. Such baffles are, however, a nuisance on account of the accumulation of dust from the fire, which blocks up the passages—the blockage being difficult to remove.

According to the *49th Alkali Inspector's Report for 1912*, p. 65, some trouble has been experienced in the working of these plants, due mainly to the simultaneous firing of several pans, which results in all the fires becoming hot together, and necessitates clinkering the fires at the same time.

The difference in total acidity in the chimney at different times is due to some extent to the sulphur in the coal, which comes off largely in the first fifteen to twenty minutes after stoking, especially with some of the lower grade slack. The difficulty is overcome readily by working each plant by a time-table. One fault appears to be in the construction of the furnaces to these pans, as the fire area is considerable, and this enables the men to place a large amount of coal on the fire at one time, with the result that the fire is for a time more or less "dark," and later on too hot, causing the acid to distil after becoming concentrated. If the coal were supplied oftener, and in smaller quantities, a more steady heat would result, and better work, with less loss of acid, would exist.

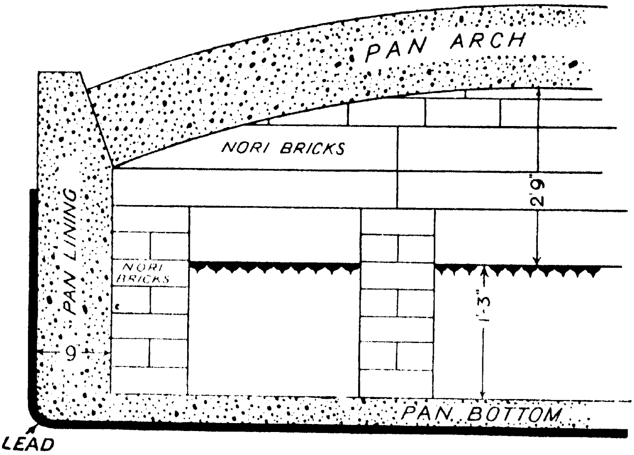

FIG. 7.

According to the *50th Alkali Inspector's Report of* 1913, considerable improvement has been noticed in the working of these plants, due to more careful firing and regulation of temperature, and the use of time-tables for firing and clinkering.

According to the *52nd Alkali Inspector's Report for* 1915, p. 73, continued improvement has been made with Hasenclever pans, by the use of double fires and smaller doors. The escape from six or eight such pans, all working to one chimney, is generally about 1 gr., or even less.

Clough (U.S. P. 15222 of 1856) proposes an over-heat pan for concentrating the acid up to 170° Tw.

Grosse-Legge[1] (Ger. P. 176370) introduces a current of hot gas tangentially to the inner side of a round evaporating dish, close to the surface of the acid, so that the gases take a spiral circuit above the acid, and escape ultimately through an exit pipe in the centre of the arch. A series of dishes may be employed and the hot air, charged with vapours, is carried off from each single dish, without getting in contact with fresh vapours within the apparatus, either in the open air or into a special flue.

Bernutat[2] (Ger. P. 281133 of 1914; B. P. 13642 of 1914) passes the acid to be concentrated through a number of compartments, connected with one another, through which hot gases are conveyed in counter-current.

Over-heat pans have also been described by Girod[3] (B. P. 17158 of 1911) and by Brunler[4] (Ger. P. 283790 of 1913).

Pipereaut and Helbronner[5] try to avoid the heavy losses due to SO_3 mist, by passing the acid in a shallow stream through a series of twelve vessels of special design in the same direction as the flue gases. Each vessel is in the form of a rectangular box, 1 metre long by 1·5 metres wide by 0·5 metre high, provided with a circular inlet and outlet—the latter a lower level than the former, and keyed together. Sodium silicate is used to make the joints tight, and the whole is covered with sheet lead, 10 mm. thick. The acid is introduced in the first vessel by a pipe in the side. Every alternate vessel is provided with a pipe, through which any desired proportion of vapour can be led away for condensation. Gas at 1200° C. can be employed directly on acid of 116° Tw., and the proportions should be adjusted so that (*a*) the concentrated acid is not heated above 300° C., at which temperature anhydride formation begins; (*b*) the gases leaving the system are still considerably below the point of saturation with water vapour. The advantages claimed are economy of fuel, low acidity of the condensed vapours, reduced atmospheric pollution, and smaller wear and tear on the plant.

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[1] *Z. angew. Chem.* (*Abstr.*), 1907, **20**, 893.

[2] *J. Soc. Chem. Ind.*, 1915, p. 611.

[3] *Ibid.*, 1912, **31**, 335.

[4] *Z. angew. Chem.*, 1915, **28**, 296.

[5] *Monit. Scient.*, 1917, **61**, 265-69; *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 6.

Lead Pans Heated from Below.

These pans are made of much smaller size than those with top-heat; the essential reason of this is the different wear and tear which they suffer according to whether they are more or less exposed to the fire; moreover, the concentration in this case is very regular, the pans being arranged usually in sets, so that the weak acid flows in at one end and runs over from one pan to another, until sufficiently strong to be run off at the other end of the set. In England long pans made in one piece are preferred, and the first portion, nearest the fire, is protected by an arch, and the larger part of the pan-bottom behind this by fire-clay slabs or metal plates. Such a pan is described fully in the second edition, pp. 664 and 665. The metal plates are covered sometimes by a thin layer of sand, in order to communicate the heat evenly to the pan; but this greatly hinders the transmission of heat. The pan is stiffened inside by iron stays covered with lead; and it is covered by an arch to carry off the vapours into the open air or into the chambers—the latter rarely.

On the Continent small pans are generally used, of 5 to 7 ft. length and width, and from 12 to 16 in. depth, of which from four to six form a set. They are made of 15 to 18 lb. lead, mostly by bending up the sides and folding over (not cutting out) the corners. Sometimes such pans, instead of being made of sheet-lead burned together, are cast about ¾ in. thick. They are in that case exposed to the fire directly, without interposing iron plates. This plan, however, is not to be recommended. Such cast-lead pans, being much thicker, are dearer than those made of sheet-lead; and they are much more liable to have unsound places, which are very soon eaten through. They are often set in steps about 2½ in. lower than the preceding one; in other cases, however, they are placed with their bottoms at the same level, but are of different depths—the pan which received the weakest acid being the deepest (16 in.), and each following one a little less, the last pan (for strong acid) being 12 in. deep. In this way the acid can flow from one end of the set to the other. At the Oker Works a long pan divided into seven compartments of equal height and level is used; the fire-grate is in the centre of one side; and the flame first passes in the centre to the back, and then returns at both sides in front of the pan.

The acid is sometimes carried over from one pan to the next by continuously acting cup-siphons. But as such siphons frequently cease to act in consequence of air getting in, owing to the slow current and the small difference of level, an overflow-pipe should always be provided to prevent the pans from running over. It is even preferable to replace the siphons altogether by overflow-pipes, which take the acid from the bottom of one pan, and allow it to run on to the top of the next one; but this arrangement requires very good plumbing work to last without continual repairs. The chamber acid is constantly running into the first pan in a regulated stream; and the strong acid runs off from the last pan without any check—the supply being so regulated that the proper strength is obtained.

The pan-bottoms are always stayed and protected from the direct action of the fire by cast-iron plates, which are thicker at the fire end than further off—say, decreasing from 2 in. down to ¾ in. Frequently, the first pan, below which the fireplace itself is built, is protected by an arch.

MacDougall[1] (B. P. 21778 of 1895) employs perforated cast-iron plates for supporting the bottom, preferably in the shape of a grid with longitudinal and transverse rills, leaving diamond-shaped holes. This plan, according to the *Alkali Inspector's*

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1895, **14**, 158.

Report, No. 31, p. 54, prevents local overheating of the *pan-bottoms, which readily occurs with solid cast-iron plates, and the pans do not show any buckling, even after prolonged use.*

Carulla[1] *interposes a copper-plate* $\frac{3}{32}$ *in. thick*, between the lead and the ordinary 1-in. cast-iron plate, which, owing to its good conduction of heat, very efficiently prevents local overheating of the lead, without interfering with the transmission of heat.

Opinions differ as to the way in which the firing of the pans should be arranged. Formerly, the usual arrangement was that of putting the fireplace under the strong pan, and allowing the fire to travel towards the weak pan, which receives it last of all. In this way the greatest heat exists where it is most required, since the concentration of the strong acid is more difficult, and its boiling-point higher, and since the cooled fire-gases serve to heat up the cold acid. When the pans are set terrace fashion, the fire takes its most natural direction, viz., upwards. Practice, however, favours the opposite plan, namely, arranging the fireplace under the weak pan, so that the strong pan is furthest from the fire. In this case the strong pan, which is otherwise worn out very quickly, suffers hardly more than the others, and the evaporation still goes on at a satisfactory rate, although there may be a little more fuel used than with the other arrangement, which is more rational as an evaporating plant, but less adapted to the special needs in this case.

Bode gives the temperatures and strengths of the acid during concentration in pans in which the acid and fire-gases travelled in opposite directions. Set of four pans:—

Acid Running in.	1st Pan.	2nd Pan.	3rd Pan.	4th Pan.
Temperature 20° . .	52°	78°	120°	138° C.
Strength 106°	...	...	...	144° Tw.

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[1] *J. Soc. Chem. Ind.*, 1893, p. 15.

Bode cites also the temperature and strength of the acid *in a set of six pans, where the fire travelled in the same direction as the acid*:—

Acid Running in.	1st Pan.	2nd Pan.	3rd Pan.	4th Pan.	5th Pan.	6th Pan.
(1) Temperature 25° .	112°	150°	160°	148°	145°	143° C.
Strength 110° .	113	120	128	134	140	144° Tw.
(2) Temperature 24° .	110	145	156	145	142	142° C.
Strength 110° .	113	118	126	134	140	144° Tw.

Here the hottest fire is the third; so that the heat of the fire-gases is utilised inefficiently. According to his experience this set required more than 20 parts of coal to produce 100 parts of acid of 144° Tw.; whilst in the set illustrated below, Figs. 8 to 11, where the fire-gases meet the acid, only 15 to 16 parts of coal were used (on the average of several years). For each ton of strong acid in twenty-four hours, about 20 superficial feet of pan-bottom may be reckoned; the whole set, therefore, furnishes 6½ tons every twenty-four hours.

Figs. 8 to 11 represent the set of pans designed and constructed by Bode, where the fireplace is outside in order to save the first pan. From this, by means of a pan area of 118 superficial feet and a fire-grate of 6½ superficial feet, 5 tons of strong acid could be produced every twenty-four hours, with a consumption of 12 to 14 per cent. of coal. According to Hasenclever, it is well to regulate the working of the pans by thermometers, in order to avoid any risk of damaging them.

According to Scheurer-Kestner,[1] four pans 6 ft. 6½ in. by 3 ft. 11 in. each, permit the concentration from 109° to 152° Tw. of sufficient acid to produce 3 tons of concentrated acid daily, with a consumption of no more than half a ton of coal.

Junge[2] describes the bottom-fired pans as used at Freiberg. They are about 6 ft. 6 in. long by 3 ft. 3 in. wide, and 8 in. deep. They are supported by ⅞ in. cast-iron plates, and arranged in tiers, the fireplace being underneath the strong bottom pan, and the acid running in at the top pan. These pans furnish a uniformly strong acid, and consume only two-thirds as much

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[1] *Wurtz. Diction. de Chim.*, 8, 159.

[2] *Jahresber. Berg u. Hutten. Sachsen.*, 1892; *Z. angew. Chem.*, 1893, p. 61.

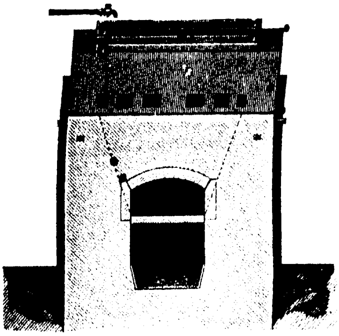

FIG. 8.

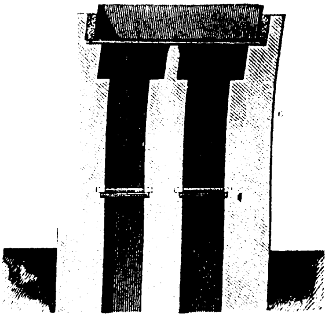

FIG.

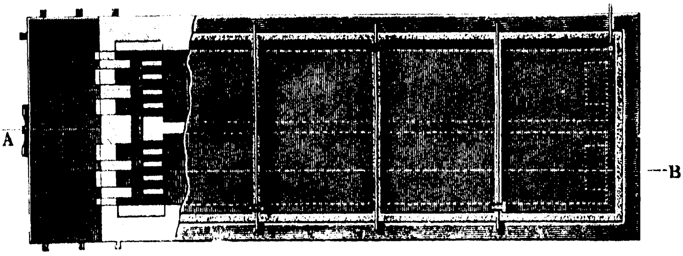

FIG. 10.

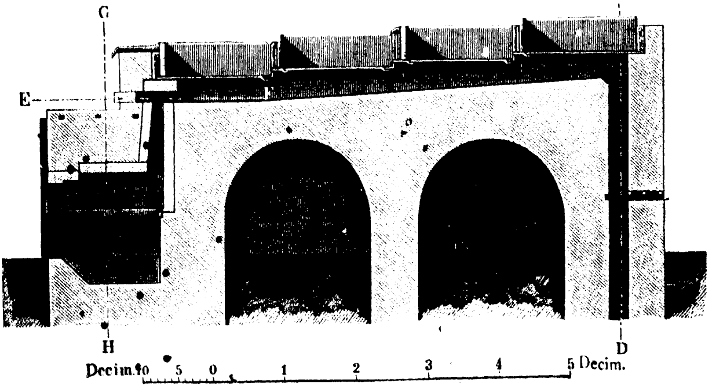

FIG. 11.

fuel as the steam pans. They suffer, however, from the disadvantage that the first strong pan is quickly worn out.

Wolters[1] (*B. P. 18834 of 1893; Ger. P. 73689*) carries the evaporation in lead vessels beyond the usual extent, preventing the action of the acid on the lead by saturating the acid with lead sulphate. An excess of this is put in acid, and kept in suspension by mechanical stirring. Most of the dissolved lead sulphate crystallises out on cooling, and can be used over again.

The Zeitzer Eisengiesserei[2] (Ger. P. 99768) employs a cylinder of antimony lead heated inside by fire-gases, and fitted on the outside with a number of antimony lead dishes, arranged so that the acid overflows from each dish to the lower one.

Lead Pans Fired by Waste Heat.

Lead pans heated from below are now seldom built as a separate unit, but as a means of utilising the waste heat from other types of concentrators—such as the cascade system (see p. 111) they have found very extensive use. The pans are built usually on the flue behind the main cascade concentrating plant, in order to make use of the heat of the fire-gases passing away to the chimney, which would otherwise be lost.

Fig. 65 on p. 134 shows the arrangement in general use.

About 25 sq. ft. of heating surface is required per ton of 140° Tw. acid produced. By this method weak acid can be concentrated up to 140° to 144° Tw. in an efficient and economical manner. It is claimed that an increase in production of 40 to 50 per cent. can be obtained by feeding cascade basin concentrators with hot acid of 140° Tw. as compared with cold 110° Tw. acid.

Lead pans are also used to utilise the waste heat of pyrites or sulphur burners for the concentration of chamber acid; but this practice is gradually dying out, as more efficient results are obtained by utilising the heat in the Glover tower. As the practice is still in use (May 1921) in a few works, a description is included in this edition. The pans are not set directly over the burning pyrites, nor even with merely a metal plate between, but are separated by a brick arch. In most cases a gas flue is placed immediately over the burners, serving at the same time as a dust chamber, on the top of which the acid pans are placed. Sometimes, from fear of leakage from the pans into the burners, they are not placed over these, but upon a continuation of the gas flue. Hasenclever even advises building a second gas flue to be used during the time when the pans have to be repaired. The heat of the kiln gas in this case is not turned to account so well as if

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1894, 13, 887.

[2] *Fischer's Jahresber.*, 1898, p. 328.

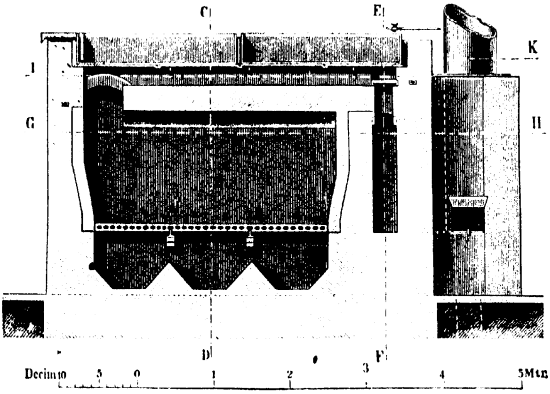

FIG. 12.

the pans stood directly upon the burners; and the latter plan can be employed all the more safely, if the danger of leakage into the burners is avoided, by providing the metal plates on which the pans rest, with a flange all round and an overflow for any acid collecting in it, like those used in nitre ovens. Leakages occur also less easily where the pans are very shallow, so that the depth of acid is only a few inches. On the other hand, it has been noticed that sometimes, especially in the case of poorer ores, the pans on the burners abstract too much heat from these to be conducive to good burning. For this reason they have been abolished at the Oker Works.

The diagrams, Figs. 12 to 18, represent pans designed by Bode, together with the pyrites kilns used by him. The

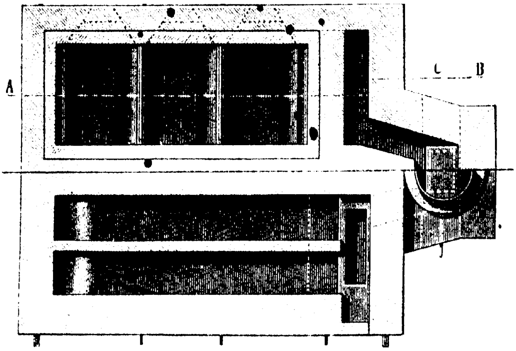

FIG. 13.

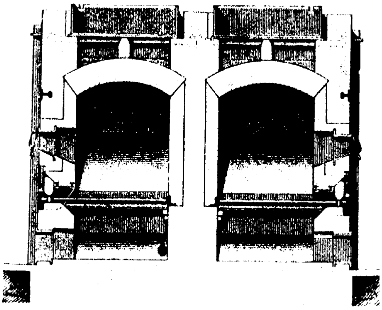

FIG. 14.

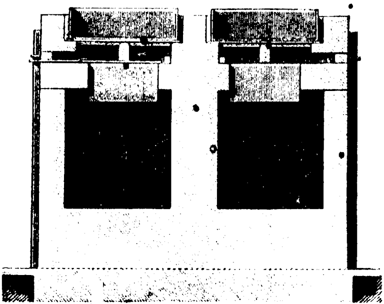

FIG. 15.

apparatus shown here belongs to a set of chambers of 40,000 cub. ft. capacity; and each burner receives daily 16 cwt. of pyrites containing 42 per cent. of sulphur. The grate of each burner has a surface of 34·4 sq. ft.; the grate bars are

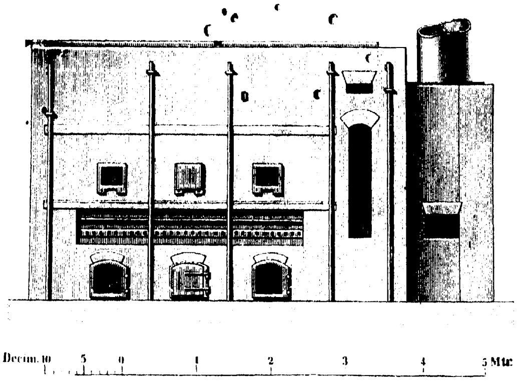

FIG. 16.

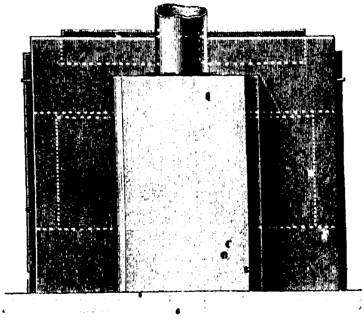

FIG. 17.

elliptical, 3 in. by 1½ in., each of them movable; the arch is 4 ft. 4 in. above the grate, with a spring of 7 in. The diagrams show how each burner can be cut off separately. The pans are 6 ft. 3 in. by 4 ft. 2 in. by 1 ft. 2 in.; made of sheet-lead weighing 8½ lb. per superficial foot. They supply daily, when 1½ tons of pyrites is burned, altogether 2¼ tons of 144° Tw. acid (*i.e.* ⅓ ton in excess of the chamber make); but, as it is necessary to evaporate 15 to 18 cwt. daily for the Gay-Lussac tower, the excess causes no inconvenience. Each year three new pans used to be put in, a pan never being left until actually burned through, but replaced as soon as the lead had become thin—a plan to be recommended thoroughly in all cases. The renewal only refers to the strong acid pans; those for weak acid are hardly injured at all. The former are therefore much better made of thicker lead—say, 30 lb. to the superficial foot, in which case they last for about two years.

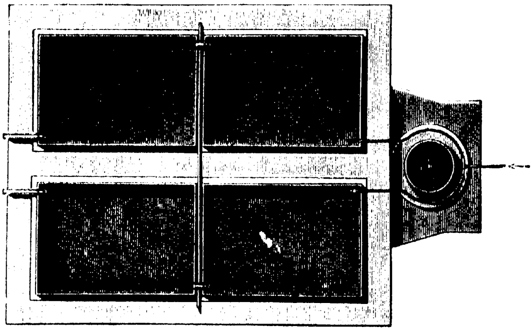

Fig. 18.

Bode gives the temperatures and strengths for a set of three pans heated by pyrites burners:—

Acid running in (heated previously).	1st Pan.	2nd Pan.	3rd Pan.
Temperature 70°	105°	128°	147° C.
" 57°	92°	106°	125° C.
Strength 106°	...	...	144° Tw.

In the case of brimstone burners, it is equally possible to employ their heat for concentrating chamber acid. In this case the burners are not covered with an arch, but with 1-in. cast-iron plates; and the shallow-lead pans are placed immediately above these.

Zanner[1] (B. P. 2379 of 1902; U.S. Ps. 693635 of 1902; 768108 of 1904) employs cast-iron pans lined with acid-proof slabs set in asbestos cement, in the flues leading gases from the pyrites kilns, the temperature of which is about 400° C.

According to information supplied by the inventor (1902) a set of two pans, 1900 × 400 mm., is capable of supplying 4 tons of acid of 168° Tw. per twenty-four hours from a mixture of 80 per cent. Glover tower acid and 20 per cent. of chamber acid. The acid obtained is clear, but slightly yellow, and the only expense is the cost of renewing the pans.

Figs. 19 to 21 show this apparatus.

In the flue (*d*), on iron bearers (*c* and *b*), rest the cast-iron pans (*a*), lined with stoneware plates (*e*), cemented with asbestos and silicate of soda. The size of the plates is chosen in such a manner that the joints are covered by the upright stone plates (*g*), which hold down the bottom plates in their places, and which cause the acid to run in a zigzag stream by the openings (*i i*)—*cf.* sectional plan, Fig. 21. The corners are secured by stones (*f f*), so that no primary joints are exposed to the acid. The pans, covered by plates (*o*), with holes (*n*), are protected against flue-dust by caps (*m*). Where acid of 96 to 97 per cent. is to be made, several pans are combined; the first of which has no stoneware lining on its bottom. The acid is fed by the porcelain-lined iron tube (*h*), and it leaves by the cast-iron lip (*k*), lined with stoneware, passing through the brickwork (*l*). The steam and acid vapours pass along with the pyrites-kiln gases into the Glover tower. It is best to provide a bye-pass for the kiln gases, for the purposes of cleaning or repairing the pans. Zanner[2] defends his plan against objections made to it by Hartmann and Benker.[3]

A new patent has been taken out by Zanner (see p. 163) which supersedes the above. Meyer[4] describes these pans of Zanner, and gives details of results obtained in working them.

W. R. Quinan[5] (U.S. P. 699011) constructs behind the pyrites kilns a "mixing chamber," provided with an iron roof, covered with infusorial earth, or the like, which, near its top, leads to an ascendingly-inclined flue, the bottom of which is formed of steps made of volvic lava. These steps possess upwardly-extending flanges at the back and sides, and a

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1902, **21**, 476.

[2] *Z. angew. Chem.*, 1907, p. 8.

[3] *Ibid.*, 1906, p. 566.

[4] *J. Soc. Chem. Ind.*, 1903, p. 781.

[5] *Ibid.*, 1902, p. 772.

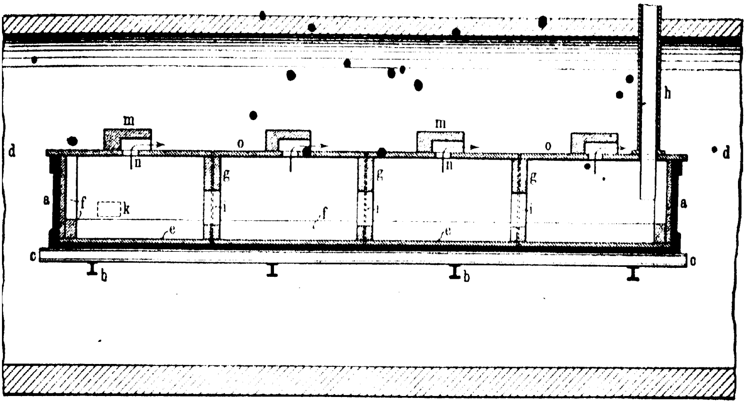

FIG. 19.

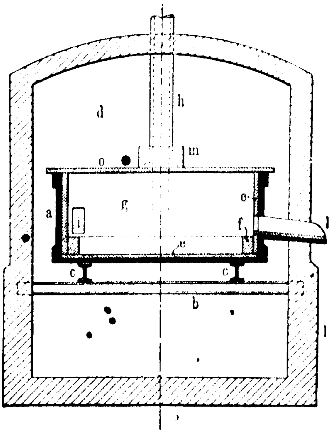

FIG. 20.

downwardly-extending lip or flange at the front end, overlapping the back flange of the next lower step. This inclined flue may be connected directly with the first chamber, or, preferably, with the Glover tower, from which the acid runs down the volvic steps, and arrives in a highly concentrated state in the mixing chamber. The partial utilisation of the heat of the gases does not at all prevent their employment for working the Glover tower, and where acid is required of purer quality than can be obtained from the Glover tower, it is the cheapest method.

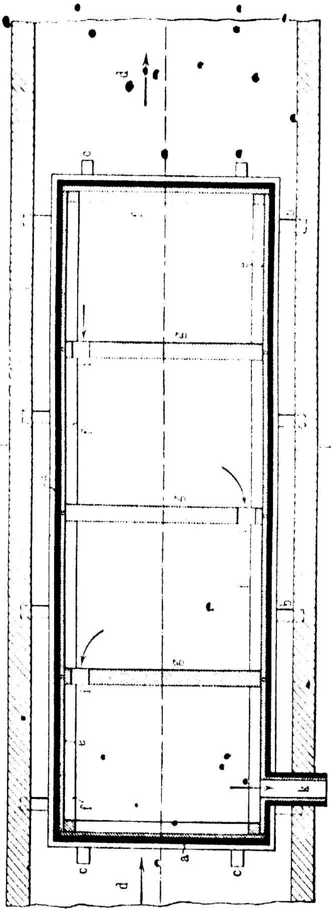

FIG. 21.

Lunge[1] states that this combination is carried out in several places in America, where the Glover tower denitrates and concentrates all the acid destined for the working of the Gay-Lussac tower, whilst the acid for sale is concentrated up to 140° Tw. in lead pans placed on the top of brimstone burners.

Proelss (U.S. Ps. 963174, 963175 of 1910; 989537 of 1911) describes an apparatus for making concentrated sulphuric acid, comprising a denitrating chamber, a concentrating chamber, and cooling apparatus, conduits for passing burner gases into the chambers, and for discharging the gases from the chambers into cooling apparatus. Lead chambers receive the gases from the cooler.

Newman (U.S. P. 1294525, 18th February 1919). The acid to be concentrated, which may be of a strength of 140° Tw., is distilled, and the distillate is introduced into the flue system from the roasting furnace to the Glover tower, so that a sufficient amount of heat is derived from the highly-heated gases in the flue system to maintain the distillate in gaseous form. The distillate is recovered in the Glover tower, or in the succeeding chambers.

Falding (B. P. 17602 of 1893; U.S. P. 541041) constructs the pyrites kilns with hollow walls, by which the air passing through is heated, and can be introduced at will below the grates. The hot burner gases are used for concentrating sulphuric acid, by passing them first into a small tower, consisting of specially acid- and heat-proof material (viz., volvic lava), surrounded by a somewhat distant lead shell, and packed with quartz. This tower is placed between the burners and the Glover tower, and receives the acid coming from the latter, which is here concentrated to 168° Tw. The gases first pass into this intermediate tower, and then into the Glover tower. Of course this acid is not pure. For pure acid the concentration in the first tower is brought only up to 71 per cent. SO_3; it is then run into iron stills (see p. 144) where pure acid up to 76·33 per cent. SO_3 distils over; while impure acid of 79·18 to 80 per cent. SO_3 (97 to 98 per cent. H_2SO_4) remains in the still, together with a mud of ferric sulphate and arsenic.

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[1] *Z. angew. Chem.*, 1894.

Concentrating Pans Heated by Steam.

According to Hasenclever,[1] the idea of concentrating sulphuric acid by means of indirect steam was first proposed by Carlier, the manager of Messrs Curtis' chemical works at Duisburg. (He seems to have overlooked Smith & Savage's U.S. P. 41647 of 1864.) After several trials at that works they ultimately employed wooden tanks lined with lead, 13 ft. square, on the bottom of which lie two lead coils, each of 150 ft. length, 1¼ in. bore, and ¼ in. thickness of lead, for conveying steam of 45-lb. pressure. The bottom of the pans is shaped like a truncated pyramid, for the purpose of more easily running off the condensed water; so that the tanks are 2 ft. deep in the centre and 1 ft. deep at the sides. The two ends of each steam-coil are connected with a lower-placed steam boiler, into which the condensed water continually flows. When the acid has arrived at 140° Tw., it is run into a leaden tank, through which a lead coil passes; the fresh chamber acid runs through this coil, and, in cooling, the strong acid gets a preliminary

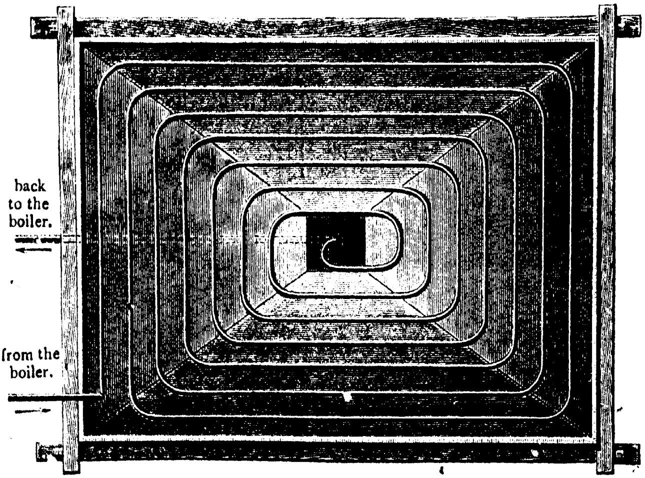

FIG. 22.

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[1] *Ber.*, 6, 504.

heating. With the above apparatus 5 tons of strong acid can be obtained from chamber acid of 100° Tw., every twenty-four hours, by the consumption of 9 cwt. of coals. The steam boiler requires only as much fresh water as is lost through leakage at the flanges, etc. It is advisable to place a wooden hood over the steam tank, to prevent any danger from acid being splashed about in case of a steam pipe bursting. Owing to the low temperature, no acid at all is evaporated; the process is very cleanly and economical as to consumption of fuel and labour. This report of Hasenclever is fully borne out by Bode.

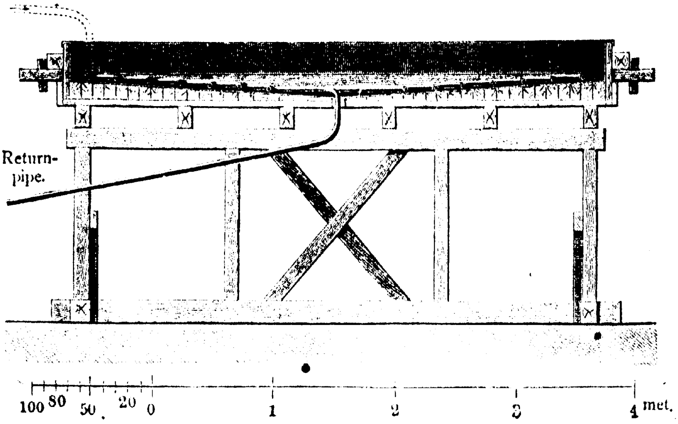

FIG. 23.

Hasenclever[1] states the corrosion of lead to amount to 0·44 lb. of lead per ton of acid. The steam pipes are mostly acted upon in the places where they dip into the acid, because the dust accumulating there raises by capillarity some acid above the level of the remainder, and this becomes too highly concentrated by evaporation. Since a lead jacket has been burned to the steam pipe at the place in question, the above drawback no longer exists.

Figs. 22 and 23 represent a similar apparatus, copied from Bode's *Gloverthurm.*, p. 27. The tank here measures 10 ft. 6 in. by 14 ft. 9 in. at the surface, 1 ft. 4 in. depth in the centre,

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[1] *Hofmann's Report*, 1875, 1, 185.

1 ft. at the sides; is heated by steam of 37-lb. pressure, and supplies in twenty-four hours 5 tons of acid of 114° Tw. with a consumption of only 8 to 10 cwt.; at others, however, from 15 to 18 cwt. of coal for the same quantity of acid.

The steam-coil must have a valve both where it enters and where it leaves the pans, which should admit of being closed from a distance in case of the coil bursting. Both the coil and the return-pipe for condensed water (for which a steam-trap should be provided) must be placed in such a way that the water cannot cause a stoppage anywhere. The lining lead weighs from 6½ to 10 lb. per superficial foot. It is very important to place the outlet for acid in such a position that the steam-coil remains completely covered when running off the acid, and is never exposed to the air, which would greatly injure the lead. After a year's work the steam-coil ought to be replaced by a fresh one, even if not showing any outward damage.

Some manufacturers avoid running the condensed water back into the boiler, lest the latter should be damaged by any acid getting into it, or even caused to explode; in such cases the above-mentioned larger quantity of coals is used. Bode points out that there is no danger of acid getting into the steam boiler, because in case of the steam boiler bursting, the steam blowing off will prevent the acid from entering the boiler. The return-pipe must not end below the water-line, but in the steam-dome.

Dr Stahl recommends employing steam of no more than 30-lb. pressure, in order to reduce the danger of bursting pipes to a minimum.

Several new steam concentrating-apparatus for sulphuric acid have been introduced in connection with ice-making apparatus, all of them founded on the principle of the multitubular boiler. We mention of these the apparatus of Kux (Ger. P. 31277), Fig. 24. The upper part (*a*) and lower part (*b*) are connected by many lead pipes (*c c*); through these and the outside pipe (*d*) the acid circulates. The whole system is surrounded by a shell (*e*), into which steam is introduced through *f*, the outlet being at *g*. The weak acid is introduced at *h*; the concentrated acid flows away at *i*; pipe *k* takes away the vapours, and a water-pipe (*m*) with an inner pipe (*l*), perforated by many holes, condenses any acid carried over.

Egells (Ger. P. 31620) describes a very similar apparatus, in which the tubes are placed in a horizontal direction, and special precautions are taken against any sagging of the tubes (*c*).

Kurtz (Ger. P. 37713) employs lead pipes provided with inner iron pipes. A combination of leaden pan with evaporating worms placed sideways of it forms the subject of a patent of the International Vacuum-Eismaschinenverein[1] (Ger. P. 38015).

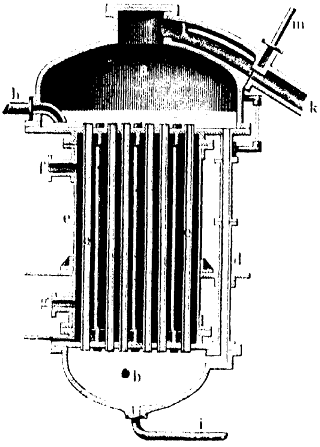

FIG. 24.

Kurtz (Ger. P. 38018) describes a steam-heated pan with counter-current.

Solvay & Co. (Ger. P. 54730) promote mechanical circulation in such a pan by a mechanically driven screw-wheel.

Junge[2] describes in detail the steam-heated acid pans employed at Freiberg. They are flat-bottomed boxes, lined with 5 mm. lead, about 10 ft. by 4 ft. 3 in. and 14 in. deep, with a coil of lead pipe, 1⅛ in. bore, $\frac{5}{16}$ in. thick, 184 ft. long, resting on loose pieces of lead piping. Six of these pans are combined in a set, communicating by overflows; the acid runs in at one end and runs out at the other. The steam pressure is not allowed to exceed 2½ atm. The temperature rises in the first pan to 125°, and does not go above 128° in the last. The strength of the acid (entering at 110° Tw.) in the six pans is respectively: 119° Tw., 127° Tw., 132° Tw., 137° Tw., 140° Tw., 143° Tw. Hence a comparatively low pressure, far below the boiling-point of the acid, suffices for concentration; but this involves slower work and much more plant than concentration by direct firing. The cost of repairs is slight so long as the apparatus is new, but subsequently it is very considerable. The thickness of the steam-coils corresponds to a strain of 60 atm. in the cold; in spite of this they later on became bulged out and burst with a pressure of only 2½ atm. This is caused partly by the action of steam from within and hot acid from without; partly by the gradual diminution of the tensile strength of the lead used at that high temperature. Lead alloyed with 1½ per cent. antimony (hard lead) cannot be used, as it is quickly destroyed by hot sulphuric acid. This occurs chiefly in the places where the hard lead is in contact with soft (pure) lead, and galvanic action sets in; but this is noticed only at higher temperatures, not with apparatus worked at the ordinary degree of heat. The steam-pans are gradually very much impaired in their efficiency by lead-mud, etc., settling between the coils; they then furnish less and weaker acid. Hence their use cannot be recommended, except where it is absolutely necessary to avoid any injury to vegetation, which is certainly altogether excluded here, as well as any loss of acid. But they are far more costly, both to erect and to work, than directly fired pans.

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[1] *Fischer's Jahresber.*, 1887, p. 508.

[2] *Jahresber. Berg- u. Hütten. in Sachsen*, 1892; *Z. angew. Chem.*, 1893, p. 61.

Evers (Ger. P. 176369) concentrates sulphuric acid (or nitric acid, etc.) in a vessel, on the bottom of which there are two coils, arranged concentrically in such a manner that the heating-liquid flows through them in succession.

The Norsk Hydro-Elektrish Kvaelstofaktieselskabet (Fr. P. 459092) runs the acid through a tower heated by steam, and removes the water from the acid in three stages, by employing steam of 3, 4, and 5 atmospheres' pressure. Steam of 3 atm. produces acid of 65 to 75 per cent.; steam of 4 atm., acid of 74 to 80 per cent.; and steam of 5 atm., acid of 80 to 85 per cent.

According to the Swiss Patent (No. 64234) of the same firm, dilute sulphuric acid is concentrated by distillation, treating the vapours with a drying agent in a drip apparatus. A cooling agent is employed at least at one point between the still and the outlet of the vapours, in such a way that the temperature in the drying zone does not exceed the boiling-point of the dilute acid.

Pritchard and the United Alkali Company[1] (B. P. 29542 of 1913) describe a tubular apparatus for concentrating sulphuric acid by means of steam, in which the joints between the projecting mantles for the tubes and the lining of the evaporating vessel, are not exposed to the steam circulating in the tubes, and where the joints of the tubes with the vessel are not in contact with the acid. This patent has not been proceeded with on a working scale.

Although the process of concentration by steam furnishes a very pure acid, it has not been found economical on a practical scale, except in connection with the recovery of sulphuric acid from the sludge acids produced in the refining of mineral oils (see p. 290).

Quality of the Lead for Sulphuric Acid Pans.

W. B. Hart[2] discusses in detail the influence of the physical condition and chemical constitution of the lead on its durability for pan-concentration of sulphuric acid. He summarises his conclusions as follows. Lead failure can originate both from chemical composition (due to imperfect desilverisation or final refining, or to the presence of bismuth, or dross, or oxide) and from the physical condition. The effects of impurities are as follows:—

1. Physically, by the formation of alloys of low fusibility and consequent local perforation of the lead, most likely owing to the presence of bismuth or tin. By leakage and consequent concentration; in such cases the action may extend even to the lead itself.

2. Chemically, at certain stages of the concentration, by strong sudden action, due to the presence of Al, Sn, or Zn, and by slow action to the presence of bismuth.

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[1] *J. Soc. Chem. Ind.*, 1914, p. 1207. [2] *J. Chem. Soc.*, 1907, pp. 504, 511.

3. Chemically, by the increased action of the acid on the lead, owing to the physical condition of the impurity, especially Zn.

4. Slow electrolytic action may set up with the deposition of certain impurities, which may accumulate and then set up physical and chemical action.

5. Antimony may have a strong and harmful chemical action, whilst copper, arsenic, and silver have little effect, and copper may even be useful under certain conditions. By constant use copper will be slowly dissolved, and its corrective effect on other impurities is then diminished or lost, so that, *e.g.*, bismuth can exert its influence more freely. This explains the failure of lead pans which have previously given good results for a long period.

6. Pure lead, under normal pan conditions, is undoubtedly less affected than the impure metal.

Failure from physical conditions may be due to faulty remelting of the lead, by use of unsuitable casting temperatures, and by severe pressure in the rolling operation, in the following way: —

1. Production of a loose crystalline structure, by casting the metal at too high a temperature, causing leakage and concomitant results.

2. By severe pressure during rolling, production of a lead surface more susceptible to attack, either temporary or constant.

3. Strong acid action in the temporary, physically altered form of lead, before the annealing effect can take place, explains the failure of pans which have been in use for a limited period.

4. The effect of altered physical conditions will extend even to lead of an exceptionally pure chemical composition.

Barrs[1] has investigated the influence of impurities in lead when heated with concentrated sulphuric acid, and has found that an increase in the purity of the lead renders it more resistant to attack by acid, even up to 280°, but recommends the addition of 0·02 to 0·05 per cent. of copper to ensure obtaining the maximum resistance.

Jones[2] gives the results of experiments carried out on the behaviour of chemical sheet-lead when heated in sulphuric acid, and concludes that, in spite of the fact that copper can function as a corrective agent and will counteract the injurious effect of antimony and bismuth, the purest lead is the most satisfactory for acid work. Pure lead is obtainable which withstands the action of hot concentrated sulphuric acid without being instantaneously dissolved when heated beyond 300° C.

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1919, p. 407.

[2] *J. Soc. Chem. Ind.* (*Trans.*), 1920, p. 221.

MacKellar,[1] as a result of plant experiments extending over several years, concludes that the protective value of copper for chamber sheet-lead has been greatly exaggerated.

Lead Testing.

The author is indebted to W. A. Calder of Messrs Chance & Hunt for particulars of the method by which all samples of chemical lead are tested before purchase. The method has been employed by them for the past eight years, with very satisfactory results, and was adopted by the Ministry of Munitions during the war.

1. The samples are first placed in order and the particulars checked; at the same time the samples are examined for any flaws, etc. If they are found damaged, a note to that effect is made. The particulars are then copied out into a book.

2. From each sample three squares (approx. ¾ in.) and one disc (approx. ¾ in. diameter) are cut; a small hole is punched in each square by which to suspend it. The disc is filed perfectly smooth and round, and all sides should appear the same.

The three squares are one each for R.O.V., mixed acid, and nitric tests, the disc for the aqua regia test.

3. The R.O.V., mixed acid, and nitric acid tests are carried out at the same time.

The strength of R.O.V. should be 96 per cent. H_2SO_4.
,, ,, Nitric Acid should be 91 to 92 per cent. HNO_3
,, ,, Mixed Acid should be 40 per cent. HNO_3, 52 per cent. H_2SO_4, and 8 per cent. H_2O.

The R.O.V. and Nitric Acid Tests.—Take three beakers (or silica dishes if a large number of leads are to be tested) and suspend the lead squares by means of glass hooks supported by glass rods laid across the top of the beaker. Take care that none of the leads touches each other. Make a chart corresponding to the positions of the various samples in each beaker, so that if any one sample should be attacked, it can be removed and the number marked off on the chart. Now, into the first beaker put a sufficient quantity of R.O.V. to well cover the samples. Into the second, a like amount of nitric acid, and into the third, a like amount of mixed acid. Suspend a thermometer in each beaker, and heat the beakers by Bunsen burners.

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1921, p. 139.

(*a*) Carefully observe the R.O.V. test to see if any samples are violently attacked up to 240°, after which continue heating to 245°, and then stop the test.

(*b*) Observe the temperature at which the nitric acid and mixed acid tests commence to boil; continue boiling for a quarter of an hour, and observe the temperature at which it boils after the quarter of an hour is up. Stop the test and examine each square to see if any appreciable action has taken place.

(*c*) If any lead fails either of these three tests, a duplicate should be done, and the failure noted in the report under the heading of "R.O.V.," "Nitric," or "Mixed Acid," as the case may be, and also under its number in the aqua regia test report.

The Aqua Regia Test.—The acid is made up as follows:—

Take 1 volume muriatic acid 28° Tw.
„ 2 „ nitric „ 100° Tw.
„ 3 „ water.

Place the water in the flask first, and then add the nitric acid; *cool* to room temperature and then add the muriatic acid. Mix thoroughly and place in stoppered bottles. Make the acid twelve hours before use, and keep in a cold place.

The filed discs are stamped on one side with the reference number; washed for a few minutes in 10 per cent. caustic soda; then well washed with water and dried in a clean towel. Three hundred c.c. of the aqua regia are placed in a 600 tall beaker standing on a gauze-covered tripod. Two discs are supported by a glass cradle in each beaker, and a thermometer (F.) suspended on a level with the leads. Heat the beakers by Bunsen burners, keeping the temperature of the several beakers the same. Make a note of the time 160° F. is reached, and continue the heating cautiously, so that it takes two minutes for every 10° F. registered. When 210° F. is reached, open out the burners full so that the maximum temperature 228° F. is reached in a few minutes. During this time (from 160° F. the leads must be constantly scrutinised, and the time that the first spots of lead chloride appear is noted for each lead) the scrutiny is kept up until vigorous action commences, and that time is noted. The test is standardised for twenty minutes from the time 160° F. is reached, and this time must be kept to. At the end of the twenty minutes lift the discs out and plunge into water, wash well, dry and examine each disc, taking into account all the data observed when qualifying the lead. From experience, the aqua regia test has been found to give an excellent guide to the probable durability of the chemical lead, and is the one on which chief reliance is placed, so that the other tests have fallen somewhat into disuse.

Concentration in Glass Retorts.

The shape of glass retorts used for concentrating sulphuric acid was introduced by Messrs Chance Bros., of Oldbury, near Birmingham. They are shown in Figs. 25 to 27. (This, together with Figs. 28-29 is taken from Roscoe and Schorlemmer's Chemistry.) These retorts consist of two separate parts—viz., a large bottle (*a*), with a neck at the top, into which fits a loose head (*c*), whose other end enters an aperture in a lead pipe or tunnel (*k*), running all along the retort house, and ultimately connected with a chimney. The bottles (*a*) are blown of thin glass, as evenly as possible, about 3 ft. high from the bottom to the top of the neck, and 1 ft. 9 in. diameter. They rest on a flat metal sand-bath (*b*), and are protected from direct contact with the flame by the round fire-clay slab (*f*). In the pipe (*k*), which conveys the condensed acid vapours to a collecting-tank, there is always some suction produced by the chimney draught at the other end; therefore the head (*c*) needs no cement to connect it with the bottle, as no vapours can get out, only air being able to enter. This is very important, as the head (*c*) has to be taken off and put on each day. The above-mentioned suction has also this effect; that retorts may continue to work with cracks in their upper parts, provided such cracks do not reach down to the level of the acid in the bottle.

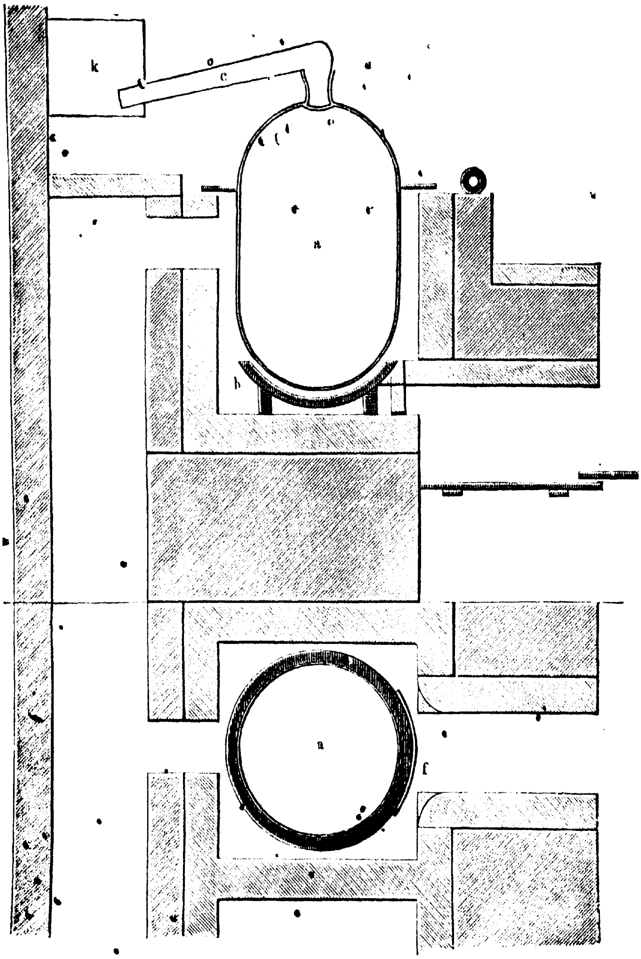

FIG. 25.

A number of retorts are always grouped together, as seen in Fig. 27, where A A A are boiling-down pans, from which the main pipe (B) takes away the hot acid of 144° Tw. On this pipe are fixed long thin lead pipes (*d d*) (Fig. 26), which are bent down at will, in order to fill the single retorts. *i i* are cooling pots for the strong acid drawn off, from which the

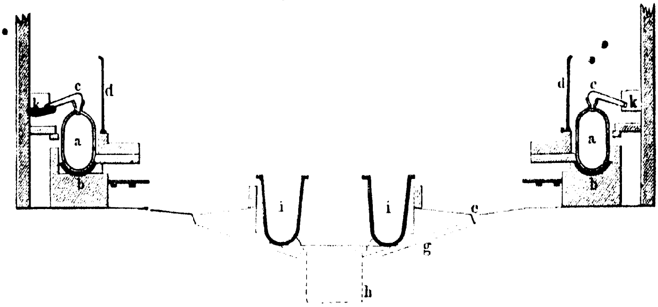

FIG. 26.

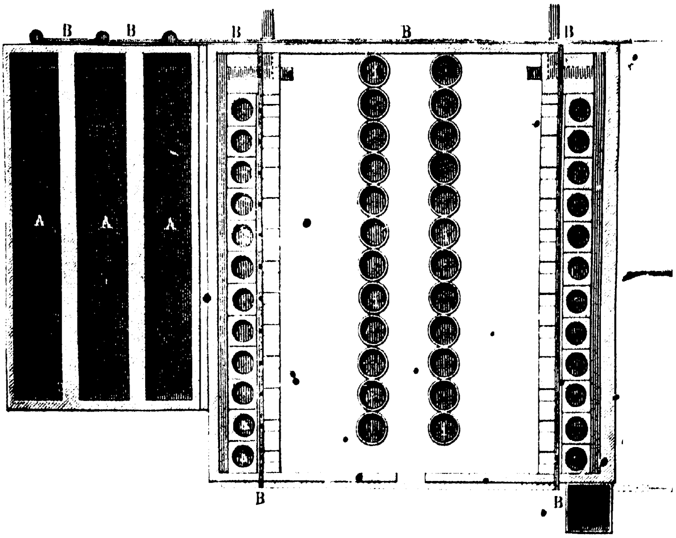

FIG. 27.

carboys are filled. The floor is made a little sloping, so that, in case of a retort breaking, the acid runs into the gutter (*e*), and from this through pipe (*g*) into cistern (*h*).

An accurate plan (to scale) of a retort setting is given in Figs. 28 and 29. This will be intelligible without further explanation.

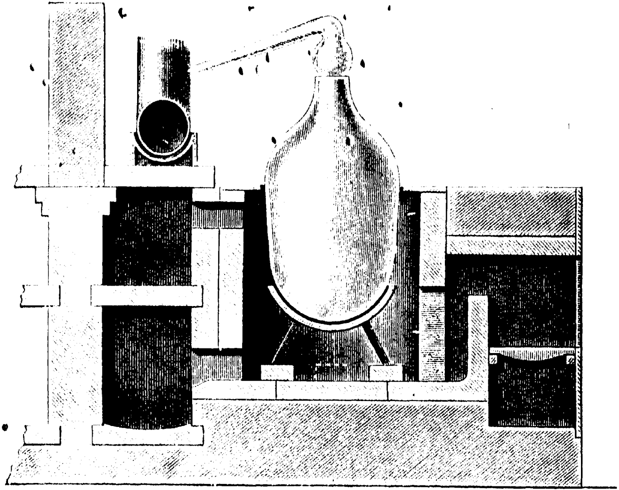

FIG. 28.

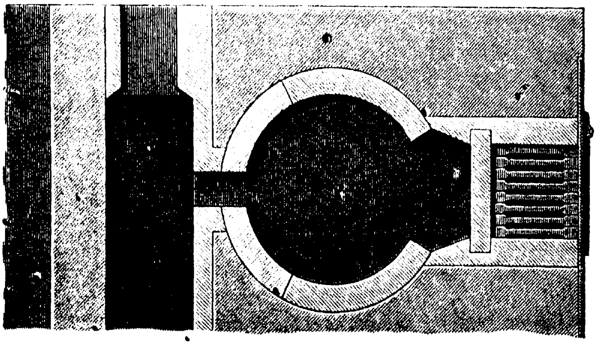

FIG. 29.

The retorts (in number from twenty to fifty) are placed in a separate house, the temperature of which is kept constantly at from 25° to 30° C.; the building being provided with tight-fitting windows and double doors; only one door is opened at a time, the other being shut so, that no draught (the chief cause of the bottles cracking) can enter. A retort-house with twenty-four retorts can turn out about 5 tons per diem. The work is carried on in this way: The distillation goes on all day long, and is finished in the evening. During the night the acid cools down to some extent; in the morning the retort-heads are taken off, and the acid is drawn off by siphons of thin lead tubing with a very narrow orifice. The siphon is filled with cold acid, and the narrow opening closed with the finger; the siphon is then put in quickly, and the finger at once washed with water. Sometimes the acid is thus drawn directly into glass carboys, but it is better to employ a series of cooling pots, as shown in Figs. 26 and 27. A small portion of acid is necessarily left in the retorts, and this is useful in refilling them with warm acid of 144° Tw., as it prevents cracking.

Fehrmann[1] describes the glass concentrating plant at Mülheim on the Rhine. The retorts had a similar shape to those used in England. The construction and working of the Mülheim plant have been very minutely described by Luty,[2] which should be consulted for further information.

A great improvement on the old plan of intermittent concentration in glass retorts is the continuously acting plan of Gridley, patented as a communication by H. Chance (B. P. 1243 of 1871). Several retorts are placed terrace-wise in an obliquely-ascending furnace, and are connected by siphons, so that the top retort is fed by fresh acid, which, after being concentrated to some extent, flows into the next lower retort, and so on. The lowest retort is placed in the hottest part of the furnace. A retort is shown in detail in Fig. 30. *a* is the head, connected with a draught-pipe common to all retorts, by which the vapours are conveyed into a small leaden coke-packed tower, and condensed by water. At *b* there is an opening in the shoulder of the retort; into this the funnel passes by which the acid enters the retort; *d* shows the level of the acid; *e* is the tubule attached to the retort, by which the acid leaves it, and *ff* show the glass connectors which convey the acid from one retort to another. The retorts are set in sand in shallow iron pots (*g*). Four beds of retorts—*i.e.* sixteen retorts, will produce 600 carboys from 6 A.M. Monday till 12 noon Saturday, equal to 46 tons, with an average coal consumption of 28 lb. per carboy of 175 lb. (equals 16 per cent.). The retorts are worked by two men (day and night turns) and two labourers.

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[1] *Fisher's Jahresber.*, 1886, p. 263.

[2] *Z. angew. Chem.*, 1892, p. 385; translated *J. Soc. Chem. Ind.*, 1893, p. 153.

The process has been further improved at the Oldbury Chemical Works by using ordinary coal-gas as a heating agent, burned in a Bunsen burner underneath each retort. This has largely increased the output and decreased the labour and breakage. The gas consumed is stated to amount to rather less than 3500 cub. ft. per ton of acid of sp. gr. 1·84.

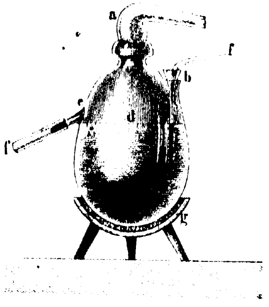

FIG. 30.

Figs. 31 to 33 show the way in which four retorts are combined in a set which is fired from a common gas pipe. The retorts are fired first till all the acid in each of them has attained full strength; then fresh acid of 144° Tw. is run into the top retort, whereupon the connecting overflow pipes begin to work, and the acid flows from each retort into the next lower one, and from the lowest into a cooler, from which it can be filled into carboys; this process goes on day and night.

A great advantage of the Gridley-Chance plan is this: that it requires no retort-house, kept at the temperature of a Turkish bath, like the old plan. It is only necessary to enclose the four retorts themselves in a glass case, similar to the vapour hoods to be found in every chemical laboratory, in order to protect the retorts against draughts. The glass case is connected by a pipe with a small leaden coke-packed tower, which communicates with the chimney; any acid vapours escaping from the retorts are condensed here.

Breakages occur rarely; but, in order to provide against this contingency, the bottom of each fireplace communicates

FIG. 32.

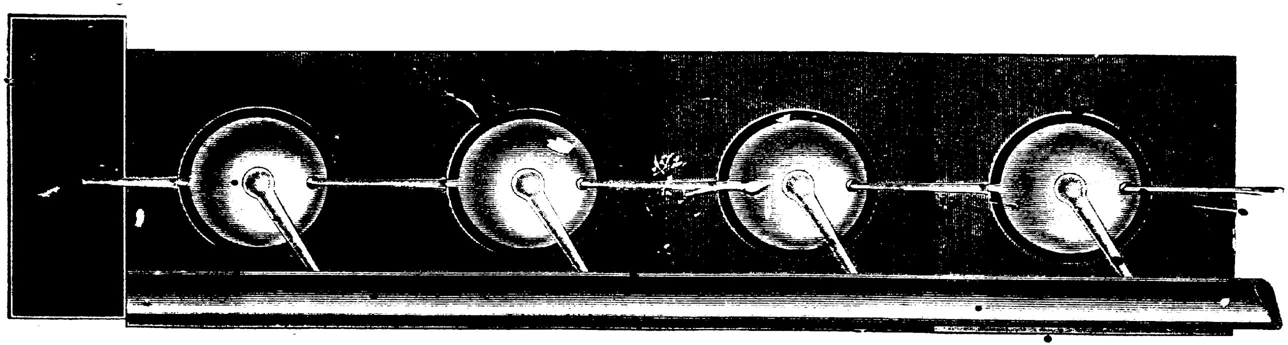

FIG. 33.

C. S. A.

[*To face page* 80.

by a pipe with an underground tank; in case of a retort breaking, the acid flows into the tank. Acid contaminated by suspended or dissolved impurities is not easily concentrated by this system, as it causes much breakage, and the strength of acid attained by this process does not exceed 92 to 93 per cent. H_2SO_4.

Carulla[1] describes an improved setting for glass retorts, which tends to reduce accidents in case of breakage.

Bowen (B. P. 2035 of 1883) describes an apparatus in which the vapours from each lower retort pass into the next higher one.

Veitch (B. P. 7901 of 1889) employs flat-bottomed retorts, arranged one above another on a stepped terrace within a tapering fire-flue common to all, the fire being placed at the lowest and widest end, and the flue narrowing upwards. The acid enters in a regular stream, travelling through the whole series. All the retorts are easily visible.

Penniman (U.S. P. 469439) employs in a set of retorts arranged step-wise, a current of air, which keeps the acid agitated continually, and so prevents their breaking.

Schofield (B. P. 19780 of 1891) describes retorts having the lower half composed of glass, and the hood of any suitable material.

The sulphuric acid vapours formed in the rectifying process in glass retorts should in no case be allowed to get into the chimney. They are partly condensed in the conducting pipe itself; after issuing from this they should pass through a small coke condenser, flushed with water, before entering the chimney to wash out all the acid. The *21st Alkali Inspector's Report*, p. 45, describes the following arrangement. The necks of the retorts pass into a lead trunk, set on a level, whose bottom is dished with an upstand of 3 in., not burned to the sides. When the glasses start boiling, a small stream of water is set running at the end of the trunk nearest the condenser, travelling in a contrary direction to the vapours; at the further end it runs out at a lip, as acid of 100° Tw. The plan is very effective, and only a small scrubber is required to arrest all the fog of acid vapour escaping from the trunk.

Prior to 1914 there was a number of works in England still using the independent retort system of concentration, and their use is noted on page 82 of the *Alkali Inspector's Report for* 1915, and in Scotland in the *Alkali Inspector's Report for* 1918.

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[1] *J. Soc. Chem. Ind.*, 1920, 21, 226.

According to information supplied to the author on excellent authority (May 1921), the concentration of sulphuric acid in independent glass retorts is carried on still in works where pure acid free from iron and lead is essential.

Pure A.R. acid is manufactured by fractional distillation, in glass retorts over an open fire, the neck of the retort passing into a suitable receiver. Latterly vitreosil retorts have been employed for this purpose, and bumping reduced by the passage of a slow current of air through the liquid.

Concentration in Platinum Stills.

The arrangement of platinum stills employed formerly is very fully described and illustrated in previous editions of this work (first edition, pp. 526 *et seq.*; second edition, pp. 695 *et seq.*; fourth edition, pp. 1129 *et seq.*). A number of data referring to the sizes, costs, and outputs of these stills is also given in previous editions, which should be consulted for detailed information. Owing to the steadily increasing rise in the price of platinum, the use of these stills has been abandoned almost entirely in favour of less costly forms of concentrators, but, for the sake of completeness, a short description is given below. The latest types of platinum stills are those of Prentice or Delplace.

The system of Prentice (Figs. 34 to 36) contains, in the place of the former circular stills, one of rectangular shape—say, 3 ft. by 1 ft. 6 in. for 4 to 5 tons O.V. per twenty-four hours. The acid enters at the back and runs out in front by an overflow. A still of this kind weighs about ½ cwt., and may be used in conjunction with platinum pans with corrugated bottoms, as shown in Fig. 34, or with ordinary lead pans. The favourable effect produced by Prentice's plan is due principally to the corrugated bottom of the pans, which increases the heating surface in the proportion of 1·57 to 1. Information regarding these stills, as used at the Griesheim works, will be found in *Chem. Ind.*, 1878, pp. 113 and 194; 1879, p. 109.

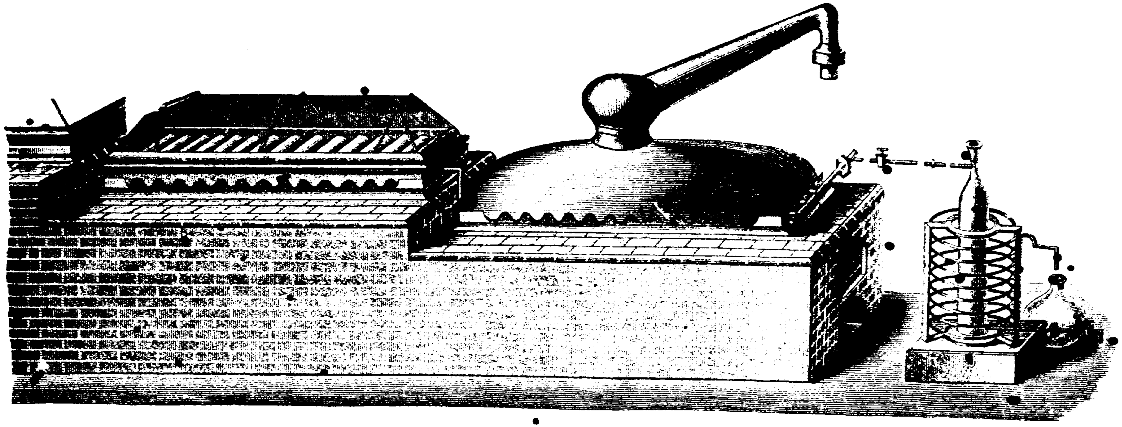

FIG. 34.

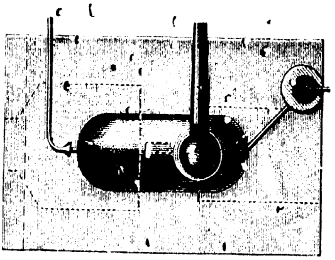

FIG. 35.

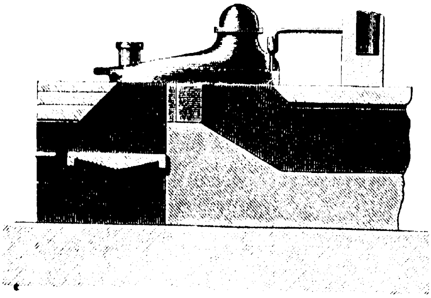

FIG. 36.

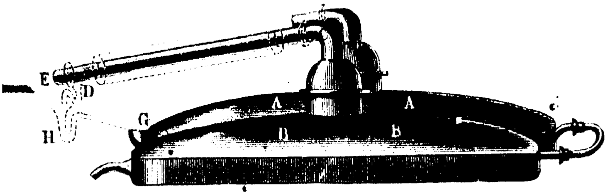

FIG. 37.

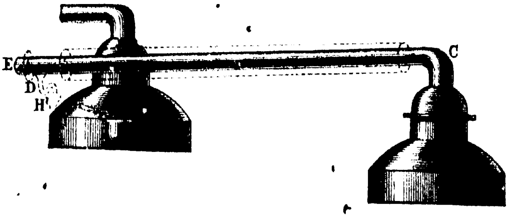

FIG. 38.

The system of Delplace[1] (Ger. P. 23159 of 1889), which was introduced into some of the largest works, is shown in Figs. 37 to 39.

In this apparatus two stills (A and B) are combined. The top still (A) is fed with acid of 144° Tw., and the distillate from the still (B). The latter, also of platinum, carries on the concentration to the highest attainable point, even up to 98 per cent. H_2SO_4, if needed. C C are heads and arms with outlet at E for the strong distillate; the weaker uncondensed vapour goes away at E. F is a bottle-shaped cooler for receiving the concentrated acid from the stills. G is a lip attached to the first still for receiving the acid from the lead pans, and the

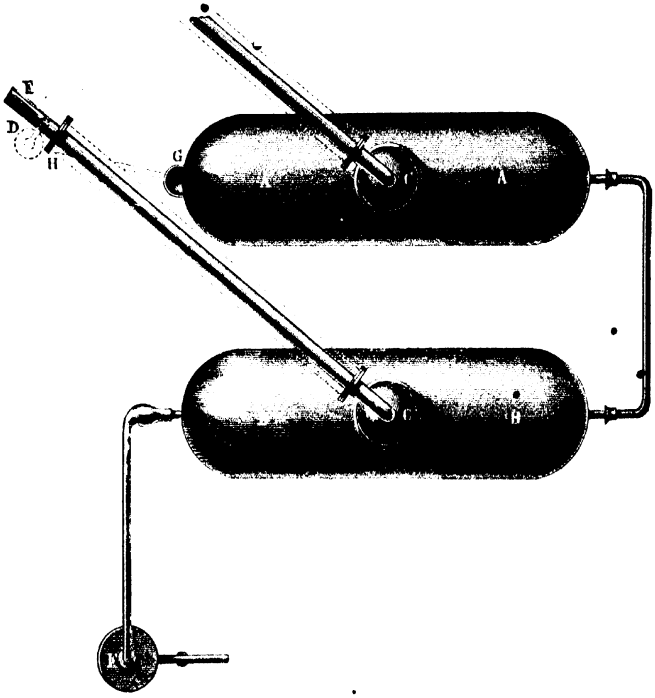

FIG. 39.

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[1] *J. Soc. Chem. Ind.*, 1884, p. 107.

distillate from B B. H is a tube for receiving the condensed distillate and carrying it back to A A. In this apparatus the acid may be brought to 79 to 80 per cent. SO_3, or 97 to 98 per cent. H_2SO_4. Instead of lead coolers, the distillate is condensed by a platinum tube 2¼ in. wide, which is cooled by water for a length of 5 ft., which permits condensing acid of any strength, free from lead. The cooling of the concentrated acid is done by an upright platinum cylinder standing in water. The acid enters at the top and leaves it at the bottom; the water enters the outer vessel at the bottom and leaves it near the top. The following advantage is claimed for the rectangular shape of still, that in working for the most highly-concentrated acid, the ferric sulphate cannot collect in the opening of the discharging pipe, which happens generally with the older type of apparatus; the distillate is said also to be weaker, the output larger in proportion to the evaporating surface, and the consumption of coal smaller than with the round shape. The apparatus is supplied by Messrs Johnson, Matthey & Company, Hatton Garden, London, W.C., by weight, at market prices for platinum. The weight of one boiler is about 50 lb.; head, condenser, and cooler together about 17½ lb. With this 5 tons of 93 to 94 per cent. H_2SO_4 are made in twenty-four hours, and double this quantity with a two-boiler apparatus.

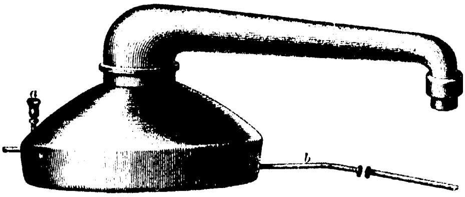

FIG. 40.

In a private communication to the author, Messrs Johnson, Matthey & Company state that the Delplace system has never been surpassed for this form of concentration, and it was only because of the introduction of the anhydrous system that these boilers were almost universally abandoned. The last new plant supplied by them was during the year 1914.

The shallow still supplied by the Paris firm, F. Desmontes, Lemaire et Cie, is shown in Fig. 40, and this is made generally with a bottom fitted with concentric partitions, which force the acid to travel through the still in a circuitous way, as indicated by arrows, and ultimately to flow through pipe *b*, as shown in Figs. 41 and 42. In order to utilise the fuel to the best advantage, many French firms employ the oblong shape shown in Figs. 43 and 44.

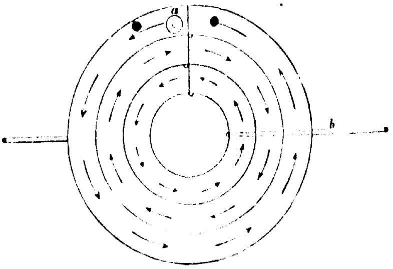

FIG. 41.

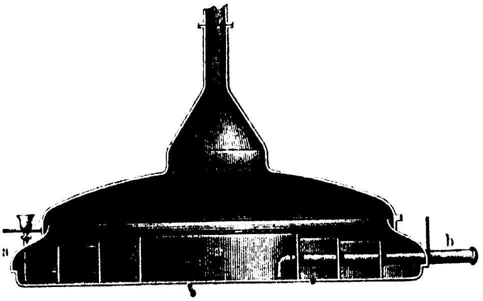

FIG. 42.

For concentrating acid up to 97 to 98 per cent. H_2SO_4, two stills must be combined, each of them heated by a separate fire, but where acid of only 92 per cent. is required, the stills may be placed on the same fire, thus saving both fuel and labour.

Scheurer-Kestner[1] gives data concerning the difference produced by working with a Desmontes' still, first without, and then with, concentric partitions—the acid being forced by the latter to remain longer in the stills in the proportion of 48 : 62.

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[1] *Bull. Soc. Ind. Mulhouse*, 1892, p. 321.

	Without Partitions.	With Partitions.
Make in 24 hours	5136 kilos	6632 kilos
Concentration of acid	92·5 %	92·5 %
Average strength of distillate . .	66·4° Tw.	16·6° Tw.
Weight of ditto	2160 kilos	2160 kilos
Weight of corresponding H_2SO_4 . .	81[illegible] "	216 "
Percentage of acid distilled . . .	15·8 %	3·2 %
Weight of coal used	1100 kilos	1100 kilos
Weight per cent. of concentrated acid .	21·4 %	16·5 %
Water evaporated	1344 kilos	1944 kilos

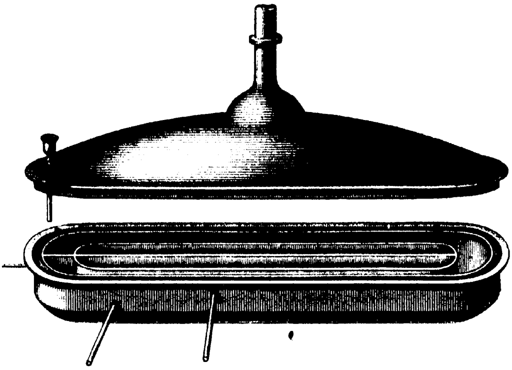

FIG. 43.

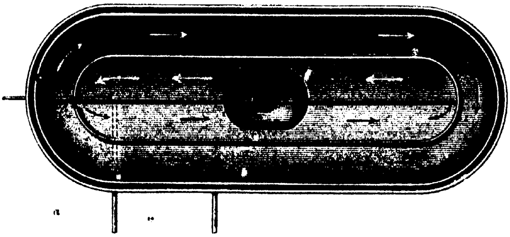

FIG. 44.

Loew[1] gives some calculations with respect to the work done by concentrating apparatus for sulphuric acid. In the case of platinum stills, the work done is in inverse proportion to the strength of the acid distilling off; the stronger the distillate, the less concentrated acid is produced, although even more fuel is consumed in the former case.

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[1] *Z. angew. Chem.*, 1896, p. 259.

Any contrivances, like Prentice's corrugated bottoms or partitions, inside a long still, which reduce the mixing of the dilute acid entering and the strong acids leaving, are useful also in this direction.

The method of firing platinum stills is of the greatest importance, not merely so far as economy of fuel is concerned, but even to a greater extent where it is necessary to manufacture acid of a regular and high degree of concentration. Ordinary hand-fired grates will do quite well where the acid need not exceed 95 per cent. H_2SO_4, and the waste heat may be utilised for bringing up the chamber acid in lead pans to the strength required for feeding the still—say, 140° Tw. But where acid of 97 to 98 per cent. H_2SO_4 is required regularly, it is much better to adopt a plan ensuring great regularity of heat. This is easy to understand, for with the very shallow depth of acid employed generally in this type of apparatus, a slackening of the fire will tell instantly upon the concentration. Assuming the feed acid to be of uniform strength (a necessary condition for continuous work), it stands to reason that the strength of acid run out in a continuous process must vary with the heat employed, and that consequently that heat should be as uniform as possible. No ordinary fire-grate will fulfil this condition; this may be done by efficient mechanical stokers, but the best method for attaining this end is the employment of a good gas-producer. One of the most efficient for the present case seems to be that of G. Liegel of Stralsund, Prussia, which has worked satisfactorily for many years with platinum stills. (This producer is fully illustrated in the fourth edition, p. 1140.)

More recently the high-pressure gas-producer of Zahn (Ger. Ps. 190660 and 237238) has been adopted with good success for concentrating plants (especially with Kessler and Gaillard plants. See pp. 168 and 195).

Concentration in Platinum Dishes with Lead Hoods.

Faure and Kessler's System.

With the ever-increasing rise in the price of platinum (see p. 102), attempts were made to reduce its use to a minimum, and stills were constructed on the principle of combining a platinum-bottom dish, as the only part of the still coming into contact with the hot concentrated acid, with lead covers cooled with water.

The most successful of these new stills was made by the firm of Faure & Kessler at Clermont Ferrand (see also fourth edition, p. 1141), and the following description has been supplied by the proprietors of the patents, Messrs F. Desmontes, Lemaire et Cie, of Paris.

Fig. 45 gives a general sketch of the apparatus on a scale of $\frac{1}{25}$. *a* is the platinum basin, with the lead bell *b*, which will be illustrated and described in detail further on. The dilute acid condensing on the sides and top of the bell runs away through pipe *c*. The uncondensed vapours pass away through pipe *d*, which bends downwards and dips into the condenser *e*. The acid formed here, after passing through the hydrometer cylinder *f*, runs away through *g*, together with that from *c*. The cooling-water for the bell enters at *h*, that for the top cover at *i*. The concentrated acid runs away at *k* into the cooler *l*, and from this through *m* into carboys, etc. The fire of the fireplace *n* passes either underneath another or even a third platinum basin, each of them placed so much higher than the preceding that the acid can run from one to another, or else directly under a set of lead evaporating-pans, in which chamber acid of 100° Tw. is brought up to 142°, the proper strength for feeding the platinum basins.

Fig. 46 gives a detailed drawing of the dish and bell, on a scale of $\frac{1}{10}$. *a* is the platinum basin, the size of which must be proportionate to the production intended. In order to stand the work for a considerable time, it should not be too thin; it is necessary to calculate from 2·9 to 3 kg. of platinum to each ton of 94 per cent. acid made in twenty-four hours. For instance, a basin capable of turning out 5 tons of strong acid per twenty-four hours weighs from 14·5 to 15 kg., and has a diameter of 0·88 m. (= 2 ft. 10⅝ in.);

for 7 tons of acid it would weigh 20 or 20·5 kg., with a diameter of 1·06 m. (= 3 ft. 5¾ in.); for 1½ tons of acid 6·5 kg., with a diameter of 0·60 m. (= 1 ft. 11⅗ in.). The rim of the basin is shaped like a hydraulic lute, *b b*, with outlet tube *c* for the dilute acid condensing on the sides of the leaden bell, *g g*; this rim is supported by a cast-iron ring, *f*. Further, there is an outlet tube, *d*, for the strong acid, and a supporting ring, *e* (of cast-iron), for the lower part of the basin. The basin is surmounted by a leaden bell, formed of a double-walled cylinder, *g g*, and a double-walled conical hood, *h h*. The cylindrical part is supported on the outside by three iron stanchions, *i i*, and an iron hoop, *k k* (40 × 5 mm.). The pieces *i i* end at the top in hooks, which serve for suspending the bell *g g*, by means of chains. The diameter of the cylindrical part is 0·870 m. (= 2 ft. 10¼ in.) inside and 0·940 (= 3 ft. 1 in.) outside. The inner shell has a thickess of 5 mm. (say, 11 lb. per superficial foot), the outer 3 mm. (say 7 lb.). Iron rods, *l l*, half an inch thick, held by means of straps *m m*, form a skeleton frame for stiffening the inner cylinders; they are from 3 to 4 in. apart. The pipe *n* serves for introducing cold water in the bottom of the annular space between the two leaden cylinders; pipe *o* conveys the partially-heated water into the annular space of the conical hood, *q q*, and *p* is the outlet for the hot water from the latter. Pipe *r* lets off the air escaping from the cooling-water during its passage through *g g*, and pipe *s* serves for the same purpose in the hood *q q*. The uncondensed vapours are taken away by pipe *u* suspended from the roof. Some other illustrations of this system are given in our second and fourth editions.

A weak part of the apparatus consists of the lead hoods. The Chemische Fabrik Rhenania (Ger. P. 64572) makes these hoods of a long coil of lead tubing, burning the walls together, so as to form a tight bell, within the walls of which the cooling water circulates. This system answers very well and has been introduced at a number of factories.

The principal feature of the work with the Faure and Kessler stills is this—that the acid, coming hot from the leaden evaporating pans, is continuously run into the platinum basin, or the first of a set of two or three such basins, where it stands in a very shallow layer (2 or 3 in. deep), and is exposed to the direct action of the fire playing upon the whole of the bottom of the dish. This causes such rapid evaporation that the acid, issuing at the side opposite to that from which it had entered and from the bottom of the still, flows out in a sufficiently concentrated state. The amount of work done is proportionate to the size and number of the platinum basins. The mixed vapour of acid and water formed in the basins, as it rises up, strikes against the water-cooled sides and top of the leaden hood, and is condensed there to dilute acid running down the sides and forming a hydraulic lute between them and the platinum dish; an overflow (at *c*) carries it outside, and prevents it from getting back into the platinum basins. The water cooling at the same time prevents the leaden hood from being damaged by the joint action of heat and acid vapours. The cost of fuel is not perceptibly different with Faure and Kessler stills from that of ordinary platinum stills; and the large quantity of water required for cooling purposes in the former system is an item of cost to be put against the initial saving in capital expenditure. It was urged by the inventors, as a great advantage of their plan, that the loss of platinum is much less than with stills made entirely of platinum; but this is very doubtful, as the wear and tear of the platinum occurs almost entirely in the places which are in contact with the fire-gases, and which are equally large in both systems; and any slight loss of platinum in the other parts of ordinary platinum stills will cost hardly more than the repairs of the very complicated leaden hood and connections of the Faure and Kessler system.

According to information from Messrs Desmontes, Lemaire et Cie, the bell and hood last about two years, and must then be replaced. The consumption of cooling water averages about 3 tons per hour, and the consumption of fuel averages from 18 to 20 per cent. of the acid made.

The great saving in prime cost caused a rapid spreading of the Faure and Kessler system, especially in Germany, Austria, and America; much less in France and England. But since the ordinary platinum stills (owing, no doubt, to the stimulus given to the makers by the new system) were considerably improved, were constructed of much lighter weight and cost for the same output as formerly, and, since the drawbacks of constant repairs, of the great amount of water required, and the frequently minor strength of the acid produced in Faure and Kessler stills became more perceptible, the latter system fell into disfavour again. It must not be overlooked that, the strength really attained by it rarely exceeds 93 per cent. H_2SO_4, or at the very most 96 per cent.; with higher strengths the lead hood is acted upon to a perceptible extent.

Loss of Platinum in the Concentration of H_2SO_4.

For full detailed statements regarding this very important matter, previous editions should be consulted. A brief abstract only is given here.

In the presence of small quantities of nitrogen acids, the loss is from 2 to 3 g. platinum per ton 93 to 94 per cent. H_2SO_4; in the absence of these (removed by ammonium sulphate) only a little over 1 g.; the loss is 6 to 8 g. for 97 to 98 per cent. HSO_4.

Hasenclever states the loss of platinum when using acid free from nitrogen compounds to be 0·25 to 0·97 g. per ton of acid. At the Uetikon works a Faure and Kessler apparatus lost 0·75 g. per ton of ordinary acid; when making the strongest acid the loss amounted to 10 g. per ton of acid.

Davis[1] states that the loss of platinum sometimes goes down to 0·34 g. per ton, but when making 97 per cent. acid it rises occasionally to 20 g. platinum per ton.

According to information supplied by W. C. Heraeus (Hanau) in 1902, from a collection of statements emanating from a number of firms, the loss of platinum per ton strong acid made is as follows:—

(1) Concentration to	92 per cent. H_2SO_4	from	0·18 to 0·78 g.
(2) "	93 to 96 "	"	0·30 to 1·30 g.
(2) "	97 to 98 "	"	1·90 to 3·0 g.

Contrary to the ordinary statement in chemical text-books, Conroy[2] has found that sulphuric acid, even when pure, exerts a marked solvent action upon platinum. In fact the quantity taken up by acid of 95 per cent. H_2SO_4 at 250° C. far exceeds that observed in practice. This is explained by the fact that reducing substances like As_2O_3. S. SO_2, and even N_2O_3, retard the solvent action. Nitric acid does not promote it directly, but in practice it is injurious, because it oxidises the reducing substances present. Ammonium, ferrous and ferric sulphate, sodium chloride and nitrate, have no action. The greater destruction observed when bringing the acid to higher concentration is not due to that concentration itself, but to the higher temperature necessary for it. Délépine[1] also found a very slight action of pure concentrated sulphuric acid on pure platinum foil, at temperatures of, say, 250° to 270° C., but decidedly more at the boiling-point 338° C. If the boiling temperature is raised by adding potassium sulphate, say, to 350° to 355° C., the loss of platinum amounts to 0·04 to 0·05, at 365 to 370° C., 0·12 to 0·13 per superficial decimetre per hour. Absolutely pure acid acts quite as much as that containing 0·1 per cent. HNO_3, and upwards. The presence of NH_4Cl lessens the attack sensibly.

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[1] *J. Soc. Chem. Ind.*, 1894, p. 210.

[2] *J. Soc. Chem. Ind.*, 1903, p. 455.

Délépine[2] states that, in the attack of platinum by sulphuric acid, although the presence of oxygen facilitates the solution of the platinum, it is not absolutely essential. The oxygen plays a secondary part, in that it modifies the equilibrium of the initial action of the acid upon the metal, as represented by the equation:

$$2Pt + 7H_2SO_4 \rightleftharpoons 2Pt(OH)(HSO_4)_2 + 3SO_2 + 4H_2O.$$

the reaction being regarded as reversible.

Quennessen[3] examined the behaviour of platinum (pure and technical) against sulphuric acid at 400° C. He concludes from his results that, in the case of concentrated commercial acid, the atmospheric oxygen acts as an oxidiser; but, in that of acid containing SO_3, this furnishes the oxygen. Le Roy M'Cay,[4] on the contrary, found that platinum is acted upon by boiling sulphuric acid, even in the absence of oxygen, *i.e.*, in a current of carbon dioxide. This action is prevented by SO_2. As_2O_3. or Sb_2O_3.

In Knocke's description of the Oker Works,[5] it is mentioned that formerly the platinum stills used to be fired with coal, but that wood had been introduced instead, because the still was found to be damaged by the sulphur contained in the coal. Even by the formation of carbon-platinum, the platinum may become brittle; the fuel therefore ought never to come in contact with it.

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[1] *Comptes rend.*, 1905, **141**, 886 and 1013.

[2] *Ibid.*, 1910, **150**, 104.

[3] *Ibid.*, **142**, 1342.

[4] *Chem. Zeit.*, 1912, p. 1072.

[5] *Dingl. polyt. J.*, **164**, 181.

Undoubtedly the durability of platinum stills is greatly influenced by the way they are set and worked. If the stills are placed too near the fire-grate, or if the flame is sooty, compounds of platinum, with carbon, silicon, and hydrogen, are formed, which make it crystalline and brittle, and imparts a rough surface to it. In this respect, gaseous fuel is superior to every other kind of firing. For further information see Kern,[1] Colson,[2] Schutzenberger and Colson,[3] Memminger,[4] V. Meyer.[5]

According to Heraeus and Geibel,[6] sulphur alone has no action on platinum; but metallic sulphides are liable to attack it.

Mylius and Huttner[7] state that when platinum is heated in a luminous coal-gas flame, a black layer is formed. If the carbon is now burned off in air, the metal is left in a rough and brittle condition, but without having undergone any loss in weight.

Mercury is contained sometimes in blende, etc., and may get into the sulphuric acid (see Vol. I., p. 131). If it reaches the platinum stills it may do great harm, as it may be reduced there to the metallic state. (Platinum will amalgamate with mercury only in the presence of sodium.)

The United States Bureau of Standards[8] states that there is no appreciable loss of weight by volatilisation up to 900°, but above this temperature the loss increases rapidly—most in the case of platinum containing iridium, and least in the case of platinum alloyed with rhodium.

Gold-lined Platinum Stills.

W. C. Heraeus of Hanau found that *gold* resists the boiling sulphuric acid much better than platinum, He quotes the following figures, putting the loss of weight of chemically pure platinum at 100.

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[1] *Chem. News*, 1877, **35**, 77.

[2] *Comptes rend.*, 1876, **82**, 591; 1882, **94**, 170.

[3] *Ibid.*, 1882, **94**, 26.

[4] *Amer. Chem. J.*, 1886, **7**, 172.

[5] *Ber.*, 1896, **29**, 850.

[6] *Z. angew. Chem.*, 1907, **20**, 1892.

[7] *Z. anorg. Chem.*, 1916, **95**, 257.

[8] *Chem. Trade J.*, 1916, p. 139.

Technically pure platinum	90
Alloy of 90 platinum and 10 iridium	58
Pure gold	13

which means that pure gold suffers only one-seventh as much as technically pure platinum.

Heraeus prepares platinum coated with a firmly adhering layer of gold, in the following manner (invented by his chemist, Dr Kuech). An ingot of platinum is brought up to a white heat exceeding the melting-point of gold; then a quantity of melted pure gold corresponding to the desired thickness of the coat is poured over it, and the double ingot thus formed is rolled into a sheet. Such sheets are made of the following thicknesses:—

0·4 mm. platinum.	0·05 mm. gold.
0·4 „ „	0·1 „ „
0·3 „ „	0·2 „ „

Both under the hammer and in the fire, these double sheets behave exactly like one metal; they are easily soldered with sheet platinum, by means of gold, the operation being conducted in a manner that the layer of gold is melted only at the soldering joint. These gold-plated platinum bottoms are especially useful in the manufacture of the strongest (97 to 98 per cent.) oil of vitriol, in which platinum is energetically acted upon. According to statements collected by Mr Heraeus from various firms, the loss of weight in his platinum gold stills per ton strong acid made (*cf.* similar statements concerning ordinary platinum still, p. 93) has been:

(*a*)	In the manufacture of	92	per cent. acid from	0·011 to 0·072 g.
(*b*)	„ „	93 to 96	„ „	0·030 to 0·138 g.
(*c*)	„ „	96 to 97	„ „	0·170 to 0·205 g.
(*d*)	„ „	97 to 98	„ „	0·040 to 0·260 g.

Heraeus[1] defends his system against some observations made upon it by Hartmann and Benker.[2]

The platinum gold combination may be regarded as one of the best kinds of apparatus where exceptionally pure and strong acid is concerned, both for the entire stills and for pans covered with leaden hoods. The gold coating in the former case must be extended to the whole interior of the boiler, not merely to the bottom, as otherwise galvanic action sets in at the place where the acid touches both platinum and gold.

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[1] *Z. angew. Chem.*, 1903, p. 1201.

[2] *Ibid.*, p. 1154.

The Heraeus composition is not adapted for impure acid which forms crusts, as these necessarily cause damage to the gold, and as soon as the platinum is exposed the galvanic action sets in. Otherwise it is excellent. It should be noticed that ordinary gold plating, whether by electro-plating or by the igneous method, does not fulfil the object of protecting the platinum, as practical tests have proved repeatedly. No doubt such gilding is more or less porous, so that galvanic action, with the sulphuric acid, sooner or later, sets in and injures the metal. This is not the case with the compact sheet of gold rendered completely dense by rolling the Heraeus bars to the required thinness.

According to information supplied by W. C. Heraeus & Co. in 1911, the platinum gold apparatus has been introduced into many works in Germany and in America. Formerly, the upper part of the apparatus was made of a composition of about 4 parts platinum to 1 part gold, but, in order to make it cheaper and harder, and to permit soldering it with gold, it is now made of an alloy of 90 parts gold and 10 parts platinum.

Crusts forming in Platinum Stills.

The iron salts contained in the chamber-acid in concentrating are precipitated as anhydrous ferric sulphate, which, being insoluble in strong sulphuric acid, partly attaches itself in white crusts in the vessel, partly remaining suspended in the acid in shiny flakes; the precipitate also contains a little lead. When it occurs in large quantities it may occasion stoppages of work, and also make the acid more or less unsaleable. This happens especially when Glover tower acid is used for concentration. In order to remedy this, Gerstenhofer suspended a large porcelain dish in the still by means of platinum wires, completely immersed in the acid, in which, owing to the boiling-movement, all crusts, etc., can collect. The dish is taken out from time to time, which can be done very quickly.[1] This arrangement seems to have been introduced in very few places, if at all. It is certain, however, that hardly anywhere is Glover tower acid used for manufacturing "rectified oil of vitriol" in platinum stills; and the acid for this purpose is always obtained by a preliminary concentration of chamber-acid, which has not passed through the tower, in leaden pans, either by special fires or by steam-coils, or, more often, by the waste heat of the stills themselves. In this way the acid is brought up to 140° Tw. without having been in contact with the flue dust from the pyrites burners, which contaminate it with an appreciable quantity of iron.

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[1] *Bode Beiträge*, 1872, pp. 50-51.

Even at factories where brimstone is burned, the Glover tower acid has not been found suitable for platinum stills, because it dissolves too much iron and alumina from the packing of the tower. But even with feeding acid concentrated by bottom-heat only, the precipitation of salts in the platinum stills cannot be avoided if the concentration proceeds beyond, say, 92 per cent. H_2SO_4. Wherever stronger acid is made, it becomes necessary to clean out the platinum stills from time to time, in order to avoid the formation of hard crusts, which would speedily ruin the still. This cleaning is effected by running the still as nearly dry as its construction permits, and dissolving the salts by means of hot water or hot weak acid. The following is the composition of crusts formed in platinum stills, as observed at a French works:—

	Hard Strong Crust.	Softer Crust impregnated with Acid.
Fe_2O_3 . . .	33·60	23·00
SO_3	63·20	63·60
SiO_2 . . .	...	0·20
CaO . . .	trace	1·10
MgO, Na_2O . .	"	0·85
As_2O_5 . . .	"	trace
$PbSO_4$ . . .	"	"
Se	"	"
Al_2O_3 . . .	"	"

At Stolberg alumina is found, sometimes exceeding the proportion of iron (1902).

An explosion on cleaning out a platinum still has been reported by Kuhlmann, jun. It occurred by running water upon some acid left in the still (the two strata evidently remaining separate) and starting the fire. At a certain point the two strata must have become suddenly mixed; and the explosion occurred through a violent evolution of vapour.[1]

Occurrence of Platinum.

The most important occurrence of platinum is in the alluvial sands in the Russian Ural Mountains. Prior to 1914 Russia supplied 93 per cent. of the world's requirements, but, owing to the war and the dislocation caused by the revolution, the output has declined very considerably, and other sources of supplies have been exploited energetically especially in Colombia, South America. According to the *United States Geological Survey for* 1913 (p. 1059), the production of platinum in Russia has been in troy oz. (at 31·1035 g.).

Year.	Officially Reported.	Altogether Estimated.	Year.	Officially Reported.	Altogether Estimated.
1900	163,060	212,500	1907	172,752	310,000
1901	203,057	315,200	1908	156,792	250,000
1902	197,024	300,000	1909	164,118	264,000
1903	192,976	226,000	1910	175,716	275,000
1904	161,950	290,120	1911	180,400	300,000
1905	167,950	200,450	1912	177,375	300,000
1906	185,792	210,318			

The discrepancy between the officially reported and the estimated figures is due to the tendency for private enterprises to keep their published outputs as low as possible, to avoid registration.

The latest information is given by A. D. Lumb in a Monograph on the Platinum Metals, published by the Imperial Institute (1920), to which the author acknowledges his debt for much of the data in this section.

Year.	Official Output.	Estimated Output.
1913	157,735	275,000
1914	157,182	240,000
1915	119,789	124,000
1916	78,682	90,000
1917	...	50,000

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[1] *Bull. Soc. chim.*, **88**, 50.

The world's production of crude platinum, as compiled by Lumb, from the most reliable sources, is given on p. 101.

According to J. L. Howe,[1] the estimated limits of the total world's production of crude platinum up to January 1917, were as follows:—

	In oz. (troy). Minimum.	In oz. (troy). Maximum.
Russia	7,115,482	10,128,308
Colombia	700,000	735,000
Borneo	175,000	200,000
United States	10,000	12,000
Canada	9,000	10,000
Miscellaneous	9,000	10,000
Total	8,018,482	11,095,308

Another estimate by J. M. Hill[2] gives 5,000,000 oz. as the total world's production to June 1917, which he distributes according to the uses made of it, as follows:—

	Oz.
Chemical and physical apparatus	1,000,000
Electrical devices	250,000
Catalysing	500,000
Dental uses	1,000,000
Jewellery	1,000,000
Minor uses and hoarded (balance)	1,250,000
Total	5,000,000

The Republic of Colombia, South America, is the second largest producer of platinum in the world, and in pre-war years supplied about 5 per cent. of the world's total output. These alluvial deposits have been worked extensively since the decline in the Russian supply, and in 1916 the output rose to approximately one-third of the Russian output. The following figures of the outputs of crude platinum have been compiled by Lumb:—

Year.	Oz. Troy.	Year.	Oz. Troy.
1911	12,000	1915	18,000
1912	12,000	1916	25,000
1913	15,000	1917	32,000
1914	17,500	1918	35,000 (estimated)

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[1] *Chem. and Met. Eng.*, 15th October 1918, p. 607.

[2] *Eng. and Min. J.*, 30th June 1917.

World's Production of Crude Platinum (in troy oz.).

	1910.	1911.	1912.	1913.	1914.	1915.	1916.	1917.	1918.
Borneo and Sumatra [3]	...	...	200	200	†	†	†	†	...
Burma [8]	...	38	57	58	37	18	9	4	...
Canada [1]	...	...	...	18	...	23	15	57	39
Colombia [5]	10,000	12,000	12,000	15,000	17,500	18,000	25,000	32,000	27,030
Madagascar [6]	13	3	...	...	...	...	...	...	...
New South Wales [2]	332	470	610	442	244	56	82	259	...
Russia [4]	176,334	187,008	177,596	157,735	157,182	119,789	78,682	50,000*	...
United States [3]	390	628	721	483	570	742	750	605	...
Victoria [7]	...	184	...	127	...	...	...	...	...

* Estimated. † Estimates not available.

Canada.—The recoveries of platinum at the works of the International Nickel Company in New Jersey for the years 1910-12 were 258, 666, and 497 oz. respectively, chiefly from Canadian matte.

Russia.—The *actual* productions of platinum as quoted in *Mineral Industry* in oz. were: 1910, 300,000; 1911, 280,000; 1912, 300,000; 1913, 275,000; 1914, 240,000; 1915, 124,000; 1916, 90,000; 1917, 50,000.

[1] *Mineral Production*, Mines Dept., Canada. Figures are for alluvial production only, and far below *actual* production figures, not including Ontario production from nickel matte, for which only incomplete information is available. (See p. 25.)

[2] *Annual Report Dept. of Mines.*

[3] *U.S.A. Mineral Resources*, 1917, *Geol. Survey.*

[4] *Mineral Industry.* These are *official* figures for production; *actual* production is much greater than these.

[5] *Mining Journal*, 30th November 1918, p. 700, and *Mineral Industry.*

[6] *Mines and Quarries Reports*, Home Office.

[7] *Dept. of Mines Reports* (platinum obtained from copper matte).

[8] *Records of Geol. Survey, India.*

Other beds of platinum bearing ore exist in the United States, especially in California and Oregon, and some in Canada. According to the *United States Geological Survey*, the production of pure platinum from American ores in troy oz. has been :—

Year.	Output.	Year.	Output.	Year.	Output.
1903	110	1908	750	1912	1,005
1904	200	1909	638	1913	483
1905	318	1910	773	1914	570
1906	1,439	1911	940	1915	742
1907	357	...	...	...	...

Price of Platinum.

The rise in the price of platinum since 1869 is given in the table below. The figures from 1869 to 1892 are taken from the report of Hasenclever;[1] assuming 1 mark = 1 shilling the figures for 1913 to 1921 are supplied by Messrs Johnson Matthey & Co.

Year.	Shillings.	Year.	Shillings.	Year.	Shillings.
1869	19	1888	34	1906	155
1870	19	1889	35	1907	113
1871	19	1890	61	1908	74
1872	19	1891	51	1909	115
1873	26	1892	49	1910	186
1874	26	1893	40	1911	189
1875	25	1894	40	1912	207
1876	25	1895	47	1913	185
1877	25	1896	50	1914	185
1878	26	1897	51	1915	190-200
1879	28	1898	56	1916	200-290
1880	27	1899	68	1917	290
1881	27	1900	76	1918	400
1882	28	1901	89	1919	442-512
1883	29	1902	89	1920	770-360
1884	32	1903	78	1921	380
1885	32	1904	82	1922	390-520
1886	32	1905	87	1923	460-560
1887	32				

Concentration in Porcelain Dishes or Beakers (Cascades).

Hughes (U.S. P. 339552) describes an apparatus consisting of porcelain dishes with glass heads, otherwise similar to the glass retort apparatus of Gridley-Chance (p. 79). The use of porcelain dishes was also patented in the United States by W. and H. Adams[1] in 1887.

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[1] *Chem. Ind.*, 1892.

Messieurs Ch. Negrier et Cie[2] at Perigueux (B. Ps. 4171, 14022 of 1890) constructed a furnace for concentrating sulphuric acid from 106° to 167° Tw. in porcelain capsules. The apparatus is fully described, with drawings, in previous editions, and only a short description is given below. It consists of two parallel ranges of eight porcelain capsules, each placed one above another, so that the acid overflowing from the lip of each pan flows into the lower one. The capsules are semicircular in shape (12 in. wide and 5½ in. deep). Every two dishes placed on the same level are contained in suitable pans, forming cavities of a single cast-iron plate, reaching from one side of the furnace to the other. Asbestos is interposed between the capsules and the metal pans, in order to protect the capsules and prevent bumping, which is lessened further by putting fragments of porcelain inside the capsules. In the event of a capsule breaking, its contents can escape into the fireplace through several holes left in the metal pans; when this is perceived, the feed of acid is stopped, the cover lifted, and the broken dish is replaced by a fresh one. The iron plates are shaped in such a manner that there is no communication between the space below, destined for the fire-gases, and the space above, where the acid vapours are formed, the joints being made good with a cement of asbestos and silicate of soda. When the capsules have been placed in the pans a layer of coarse sand is put into the space between them, up to the edge of the capsules. The brickwork above the level of the capsules is made of silica brick; the top cover is made of cast-iron or glass. The heat of the fire-gases issuing from the apparatus is used for concentrating the feed acid in a similar apparatus, or, preferably, in lead pans.

This system is described minutely by Kretzschmar.[3] The gases from a set of four furnaces pass underneath three sets of lead pans, where they concentrate the acid up to 134° to 142° Tw., and heat it to 145° to 149° C. Every furnace produces 25 cwt. of acid of 93 per cent. daily, with an expenditure of 23·5 per cent. of rather low grade coal.

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[1] Scheurer-Kestner, *Bull. Soc. Ind. Mulhouse*, 1892, p. 317.

[2] *J. Soc. Chem. Ind.*, 1891, **10**, 46; 639.

[3] *Chem. Zeit.*, 1892, p. 418.

Lemaitre[1] (Fr. P. 357555) describes an improved form of apparatus.

F. Benker[2] has erected in France a number of apparatus for concentrating sulphuric acid in porcelain dishes covered with a special protecting cement, and enclosed in a chamber built of volvic lava. Drawings of the plant and additional information is given in our fourth edition, pp. 1121, 1122.

A modified system is described by Hartmann and Benker[3] in which the dishes are all placed on fireclay rests, and are cemented in these with asbestos and sodium silicate, so that the fire-gases are separated completely from the acid fumes. The heating also takes place, not by means of four small fireplaces, as previously, but by a single large fireplace (26½ in. by 12½ in. grate surface), so that in lieu of coke, coal can be used for firing. There are twenty-four basins in each cascade, or forty-eight in both; and the four lowest dishes of each row are protected by a curtain arch, so that the acid boils quietly without spurting.

Beaker Apparatus.

This kind of concentrating apparatus was introduced first by Webb, and followed by Levinstein and others. The principle is quite similar to the dish apparatus, and the material used is either glass or porcelain.

Webb's B. Ps. are Nos. 2343, 17407, and 18891, all of 1891. As shown in Figs. 47 and 48, his apparatus consists of fourteen or sixteen glass or porcelain beakers (A A) arranged one above the other, about 11 in. wide and 21 in. high, with overflow lips communicating with movable tapering glass pipes, placed in a slanting position in the next lower beaker, so that the acid flows from each beaker on to the bottom of the next, and from the last of these through a cooler into storage vessels.

According to Webb (B. P. 2343 of 1891), a series of glass vessels is placed on slabs, arranged in steps, in a heating chamber; the vessels are enclosed near their upper edges in iron plates or slabs, corresponding to the bottom. In every one of these vessels, a loose tapered glass tube is placed at an

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[1] *Monit. Scient.*, 1906, **65**, 126.

[2] *Chem. Zeit.*, 1899, **23**, 147; *J. Soc. Chem. Ind.*, 1899, **18**, 371.

[3] *Z. angew. Chem.*, 1906, p. 564.

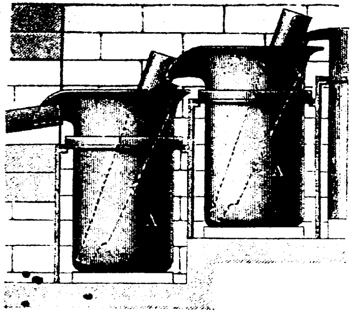

FIG. 48.

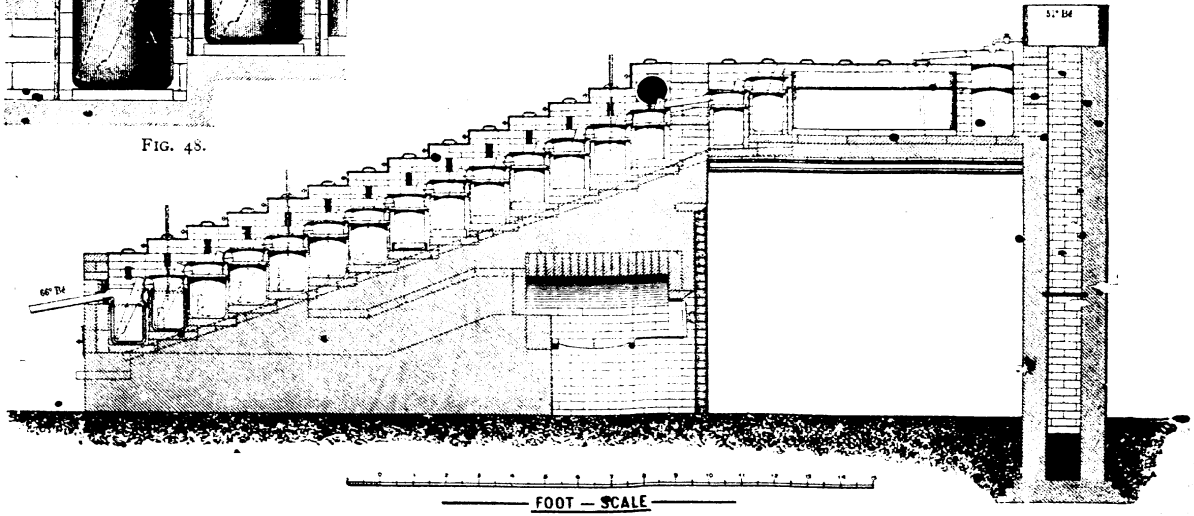

FIG. 47.

angle, reaching from the spout of one vessel to the bottom of the next lower one, where it is provided on its side with an outlet slit. The fire-gases pass first into combustion chambers on each side of the heating chambers, and from thence into space left around the glass vessels. The weak liquor is fed into the tube of the uppermost vessel, and displaces a certain amount of acid, which will overflow into the tube of the next vessel, etc., thus causing a thorough interchange in the liquor to be evaporated. The concentrated acid is delivered from the last vessel of the series. The feed of acid is regulated by means of a thermometer placed in the fourth beaker from the bottom. Two sets are usually built together, and will produce 5 to 6 tons of strong acid (1·838 sp. gr.) per week from acid of sp. gr. 1·60.

So long as all the beakers were made of glass, the breakage was very heavy; and this led to the replacement of the three bottom beakers of each set by porcelain vessels. Later on the breakage was reduced further by replacing all the glass beakers with porcelain vessels.

Webb (B. P. 29884 of 1896) describes a firing arrangement by a gas producer, where the flame does not act from the higher end to the lower, but vice versa. A further patent of Webb's (B. P. 1516 of 1901) describes double-walled beakers consisting of an outer vessel and an inner vertical vessel. This modification appears to be that which is mentioned in the 38*th Alkali Inspector's Report*, and described in the Ger. P. 135886 by F. G. Webb and Webb's Patents, Ltd. There is a stepped series of beakers, each of them containing an inner cylindrical vessel, not much narrower than the beaker itself, open at the top and communicating by holes at the bottom with the annular space between the two vessels. The acid overflows by a lip from each of the outer beakers into the inner vessel of the next lower beaker, passes through the bottom holes into the annular outer space, and overflows from this into the inner vessel below. The whole may be placed in a hot air oven; or else the top edges are formed in such a manner that a still head may be placed on each beaker, with an arm connected with a slanting draught pipe (*cf.* Gridley's apparatus, p. 79), from which the vapours are taken into a tubular water-condenser before passing into the draughting shaft; in this case the beakers are heated only in their lower part. Webb (B. P. 1515 of 1901) describes a tubular water-condenser for retaining the acid vapours.

Levinstein's patents are 19213 of 1892; 2476 and 2835 of 1893; 22844 of 1894; his apparatus is very similar to Webb's, but the beakers have rounded bottoms, and are placed in metal dishes, and the overflow pipes are modified. Furthermore, the dilute vapours from the upper portion and the strong vapours from the lower portion of the battery are carried away separately.

Quite similar to the above is Bradbury's apparatus (B. P. 22327 of 1893); J. W. Scott's (B. P. 14215 of 1894); R. Wilson's (B. P. 14221 of 1895); and Schwab's (B. P. 22512 of 1896).

H. E. Green (B. P. 27209 of 1911), in order to economise space, makes the cascade double back on itself.

MacKenzie (B. P. 6415 of 1909) provides for the dishes of cascade apparatus, air pipes for the purpose of agitating the contents of each dish, so that the impurities do not settle on the bottom, and cause overheating.

Although many plants of the Webb type were erected in England, they have been discontinued, partly on account of the excessive breakage of the breakers, partly because of the high fuel consumption, and partly because it was found impossible to prevent the escape of dense white fumes from the chimneys (which were themselves sometimes ruined by these fumes, and had to be rebuilt). The *Alkali Inspector's Reports* of several years teem with complaints of this sort. The reason seems to be the same as that quoted in the case of lead pans with surface evaporation—viz., the formation of an acid mist of tiny, liquid, vesicular drops (p. 45); or else the difficulty of condensing sulphuric anhydride.

A. Nobel proceeds on the following principle (Ger. P. 10149 of 1880). Since cast iron is not acted upon by the *vapour* of sulphuric acid, the concentrating apparatus is made in the shape of a column consisting of cast-iron pipes, in which porcelain dishes are placed on ledges. Each dish has an opening through which a glass rod reaches into the next lower dish; this is intended to prevent the acid from splashing about in its downflow from dish to dish. When all the dishes are filled, the column is heated by flues surrounding it on the outside. The acid vapour, as well as the concentrated vitriol, is taken away at the bottom.

Another kind of column combined with a system of stepped beakers is the apparatus patented by Guttmann (B. P. 16220 of 1898). He arranges glass or porcelain beakers, with overflows, in a vertical spiral column. They are placed on iron dishes, attached to curved hinged doors, which together form a vertical heating column, within which fire-gases surround the concentrating beakers. Another patent (Ger. P. 109247) of his describes an arrangement for heating up the air required for the combustion, by means of the waste heat of the apparatus.

A Guttmann concentrating tower has been erected in England, but it is fired by coke instead of gaseous fuel, and has been modified with a view to reducing breakages.[1]

Concentration in Fused Silica Ware (Quartz).

In 1839 a French physician, Gaudin,[2] succeeded in fusing quartz into a pasty condition by means of the oxyhydrogen blow-pipe; and small tubes of fused quartz were made by Gautier[3] in 1869-1878. Boys[4] (1887-1889) by a method which has become classical (the crossbow), prepared filaments of fused quartz which were used in the preparation of delicate physical instruments, such as the suspended mirror galvanometer.

From 1899 to 1901 much work was carried out on the fusion of quartz; in France by Dufour and Le Chatelier; in Germany by Heraeus; and in England by Shenstone. In 1901 Shenstone demonstrated his method of fusing rock crystal with the oxyhydrogen blow-pipe before the Royal Institution in London; and his process has been developed industrially by the Silica Syndicate, Hatton Garden, London (1910).

In 1902 the firm W. C. Heraeus of Hanau commenced to place on the market small vessels of transparent fused quartz, and in 1903 Heraeus described his methods to the 5th International Congress of Applied Chemistry. The cost of production, however, by these methods was prohibitive, unless oxygen could be obtained at a very low price; and about this time the attention of workers was directed to the possibility of using the electric furnace for fusing quartz sand.

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[1] *Alkali Inspector's Report*, No. 38, p. 128.

[2] *Comptes rend.*, 1839, **8**, 678, 711.

[3] *Comptes rend.*, 1900, **180**, 816.

[4] *Phil. Mag.*, 1887, **28**, 489.

In 1902, Hutton[1] described the preparation of tubes by the fusion of quartz sand or particles of rock crystal by means of the electric arc and resistance furnaces. These experiments mark the beginning of the fused silica industry, which was created in England by the collaboration of Bottomley and Paget, with Hutton (B. P. 10670, 9th May 1904). In 1905 Bottomley and Paget founded the Thermal Syndicate, Ltd., Wallsend-on-Tyne, for the development of their patents on a commercial scale, and their material is known under the name of "Vitreosil."

According to Bottomley,[2] the type of furnace employed is an electrical-resistance one; the heating core or resistance consisting of plates, tubes, or rods of carbon or graphite. In the manufacture of tubes or pipes, the starting point is a hollow cylinder of plastic silica, formed by fusing a mass of pure quartz sand (99·7 per cent. SiO_2) round a central core, through which the current is passed. As soon as the hollow cylinder has been formed, the heating core is withdrawn from the centre of the mass, which can then be removed from the furnace and drawn into tubing. If a moulded article is required, the hollow plastic cylinder is closed at one end by mechanical pressure, and a refractory nozzle (to which a source of compressed air is attached) pressed into the other end. The fused mass is then placed in the mould and expanded with compressed air, till it assumes the required shape.

The limits of temperature at which these furnaces can be worked are very narrow, because the temperature at which quartz reacts with carbon to form carborundum is very close to the temperature required for working the silica. The volatility of silica also presents another difficulty, as it volatilises readily at temperatures little above the melting-point. The temperature required for fusing silica is between 1800° and 2000°, and the weight of fused material which can be worked exceeds 200 lb. Even at very high temperatures silica never becomes really fluid like glass, but remains in a plastic condition, so that when large masses are fused, the bubbles of air contained therein cannot escape to the surface and so render the mass non-transparent.

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[1] *Amer. Electro-Chem. Soc.*, 1902, 2, 105.

[2] *J. Soc. Chem. Ind.*, 1917, 86, No. 11, 579.

For an excellent account of the development of the fused silica industry, see Flusin.[1] Fused silica has many valuable properties which render it of great value to the chemical industry. It is amongst the most refractory of materials, melting at about the same temperature as platinum (between 1700° and 1800°), but it begins to soften at about 1500°. The coefficient of expansion is extremely small, being approximately 59×10^{-8}, or about one-seventeenth that of glass, so that articles made of fused silica resist even the most violent changes of temperature. It has a tendency to become very brittle when subjected to a high temperature (over 1100° C.) for long periods, due to a reversion from the vitreous to the crystalline state. The specific gravity is about 2·07, and it is impermeable to all gases, with the exception of hydrogen, and that only at high temperatures.

Fused silica is unattacked by all acids, except by hydrofluoric acid and phosphoric acid, and the latter only near its boiling-point (400°), so that it is used extensively throughout the chemical industry, and especially for the concentration of sulphuric acid in the cascade plant.

Dr Wolf Burckhardt and W. Borchers[2] (B. P. 18053 of 1911) claim that the addition of oxides of titanium and zirconium to fused quartz improves its properties, and founded the Zirkongesellschaft at Frankfort-on-Main for the manufacture of these new materials called "siloxides." Pohl[3] states that the substance has no advantage whatever over vitreosil. The factory was working in 1914, but appears to have ceased in 1921.

Silicon nitride is recommended by Herre[4] as an acid-resisting material in the concentration of acids; and silicon tubes are made by the Carborundum Co. at Niagara Falls for conducting hot mineral acids.

Voelcker & Co. (Ger. P. 258351) manufacture objects of quartz glass with coloured, or completely fused surfaces by fusing quartz sand round an electric resistance core, and uniting the quartz body by blowing; the latter body has previously received the desired quality of surface or colour by suitable treatment.

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[1] *Chimie et Industrie*, 1921, **5**, No. 2, 119.

[2] *J. Soc. Chem. Ind.*, 1912, **31**, 189.

[3] *Z. angew. Chem.*, 1912, p. 1849.

[4] *Chem. Zeit.*, 1914, **38**, 317, 341.

The Aussiger Verein für Chemische und metallurgische Fabrikation (Austr. P. appl. 4345) manufactures tubes of quartz by means of an electric flame arc produced in the hollow of the tubes to be made. This hollow is shaped before producing the arc, and is kept up by it.

Vitreosil Cascade Concentrating Plant.

The development of the continuous cascade system of concentration by Messrs Hartmann and Benker has been described on p. 104.

A great impetus has been given to the more extensive use of this type of plant, by the introduction by the Thermal Syndicate in 1907, of "vitreosil" dishes and basins. There were three Benker cascade plants at work in Great Britain at this time; and the porcelain basins were replaced rapidly by fused silica vessels, with satisfactory results. According to the *Alkali Inspector's Report for* 1907 (No. 44, p. 28), the substitution of basins of fused silica for porcelain basins has been found to lessen the waste of acid and interruption of the process required for replacing broken porcelain dishes. Further improvements and economies were effected in 1910, when the Thermal Syndicate brought out an "all silica" cascade concentrator, consisting of thirty shallow tray preheaters and fifty basins, all under one flue. In recent years the tray form of preheater has been abandoned in favour of deep beaker preheaters, which have a greater heating surface, and give an increased yield.

Information on the working of this plant is given by Bottomley[1]; this has been supplemented by the Thermal Syndicate, Ltd. (May 1921).

The latest form of plant is shown in Fig. 49.

It consists of two parallel ranges of fifteen preheating beakers (S) and twenty-five basins (U) (Fig. 50), each placed one above another, so that the acid overflowing from the lip of each upper vessel flows into the lower one. The dimensions of

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[1] *J. Soc. Chem. Ind.*, 1917, 36, No. 11, 579.

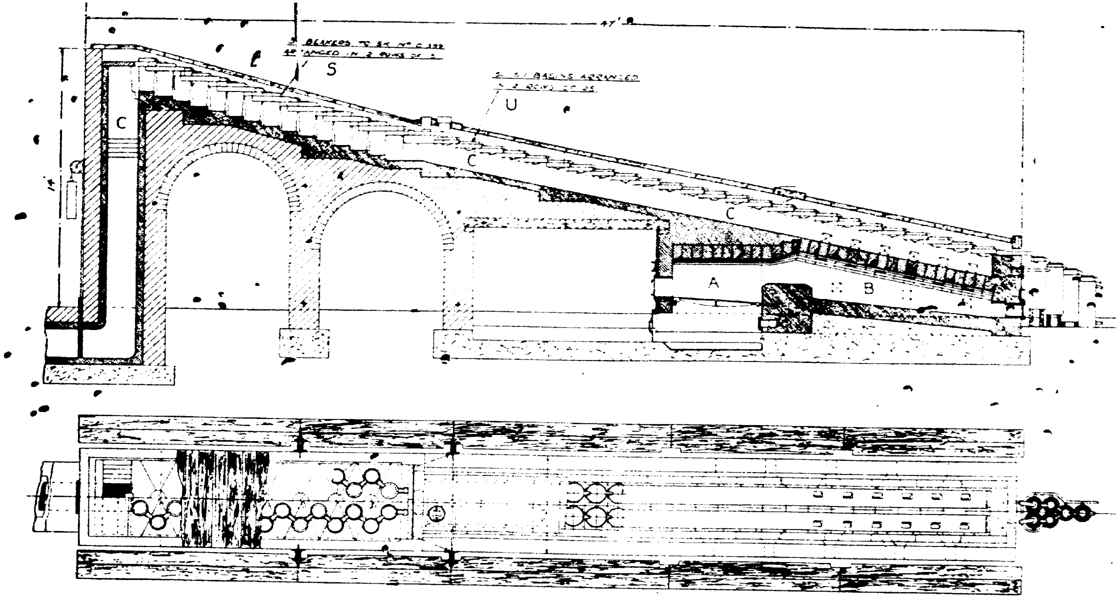
47'
14'
BEAKERS TO SK No C 132
ANGED IN 2 ROWS OF
S
BASINS ARRANGED
2 ROWS OF 25
U
C
C
C
C
A
B

FIG. 49.

the beakers are: height, 20¼ in.; diameter at top, 11 in.; diameter at bottom, 9 in.; and the basins are 12¼ in. diameter by 5¼ in. deep. The basins are made in various shapes. The vitreosil vessels are placed on special acid and heat-proof seatings recessed to take asbestos rope rings, which form a tight seating between the firing and the fume flues. From Fig. 49 it will be seen that an ordinary open fire-bar furnace (A) is fitted under a portholed firing arch (B), from which the flue (C) runs the whole length of the plant, and finally out to the chimney. The plant is fired usually with low-grade fuel, and the fuel consumption varies from 15 to 20 per cent. of the weight of finished acid produced. The fume flue is formed of acid-proof slabs built on each side of the double row of basins, and covered with acid-proof tiles. The fumes are drawn from the flue through a condenser consisting of a lead-lined box packed with coke.

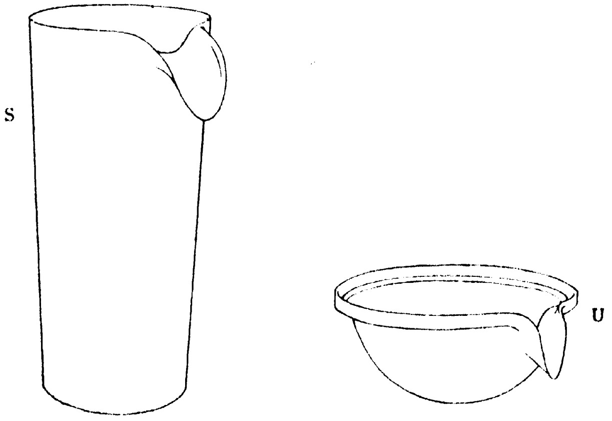

Fig. 50.

About 500 cub. ft. of condenser space will give an exit of 0·5 gr. per cubic foot for a 5-ton unit, which is the rated capacity per twenty-four hours of a standard plant commencing with cold acid at 110° Tw. The 10-ton units are merely two 5-ton sets built together with an 8-in. dividing wall, and fired separately.

Steam jets or fans are not required to create draught, as the ordinary chimney draught, providing about $\frac{5}{8}$ in. water suction for both firing and fume flues, is sufficient.

The cooling of the concentrated acid from the lowest basin is carried out by six silica pot type coolers which consist of an outer lipped vessel and an inner centre pipe. The outer vessel is water-jacketed, and the hot acid entering the centre pipe descends to the bottom, and, passing through slots in the pipe, rises between the pipe and the walls of the vessel, where it is cooled by the circulating water outside to a temperature of about 200° F., when the final cooling can be performed more satisfactorily through a lead coil. The acid does not come into contact with any other material than fused silica during its passage through the concentrator, and hence the plant is adapted specially for the concentration of pure water white acid.

A comparison of the results obtained with the two types of preheaters is given by the Thermal Syndicate, as follows:—

	Plant with Trays (Single unit.)	Plant with Beakers (Double unit.)
Inlet of trays	20° C. 106° Tw.	33-37° C. 106° Tw.
Outlet of trays	112° C. 110° Tw.	172° C. 130° Tw.
Outlet of basins . . .	168° Tw. (at 15° C.)	168° Tw. (at 15° C.)
O.V. made per 24 hours . .	4 tons.	10 tons.
Fuel used per ton O.V. . .	4½ cwt.	4 cwt.

In the second set, beakers Nos. 12 to 15 had to be enclosed and connected to the fume flue, as the acid was boiling, and fuming taking place.

The claims made for this type of concentrator are—(1) ease and speed of construction; (2) low initial and maintenance cost; (3) fuel economy; (4) continuity of working; (5) no steam jets or fans to create draught; (6) water white quality of acid.

According to information supplied in May 1921, upwards of 1250 5-ton units have been supplied to acid manufacturers all over the world, including the large Government and trade explosives factories in the United Kingdom and in the Colonies, France, Italy, America, Japan, Russia, Mexico, etc., for the

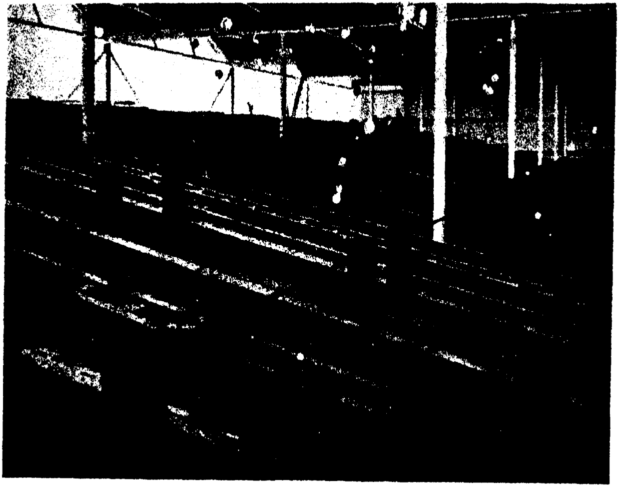

FIG. 51.

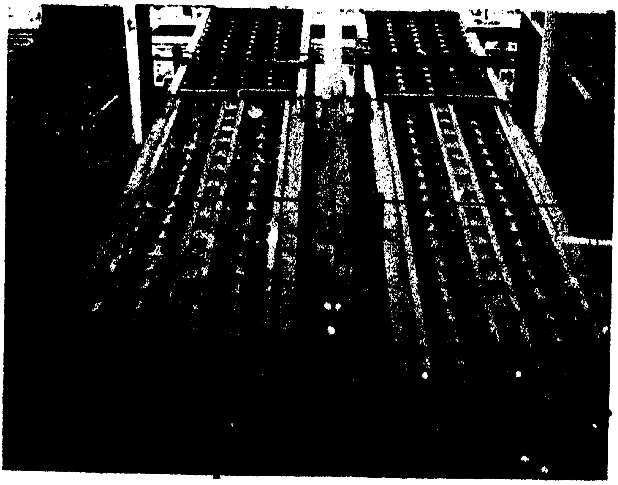

FIG. 52.

concentration of chamber acid, reconcentration of residual acids from nitration processes, and recovery of sludge acids from mineral oil refining.

Obsidianite Seatings for Cascade Plants.

The use of "obsidianite" for the fire- and acid-proof seatings, side slabs, and covers, has contributed towards the success of the vitreosil cascade system. This material is manufactured by Messrs Charles Davison & Co., Ewloe Barn, Chester, and has been used extensively in many chemical works, with satisfactory results. Obsidianite is a hard, vitreous, non-absorbent material, impervious to acids of all kinds, and very durable and dense. An analysis supplied by the makers is given below:—

Silica (free and combined)	79·1
Alumina	15·2
Iron oxide	3·5
Lime	1·2
Magnesia	0·3
Alkalies	trace
Organic matter, loss, etc.	0·7
	100·0

In addition to its acid-resisting qualities, obsidianite will also withstand temperatures of 1500°, so that it is very suitable for use in sulphuric acid concentration plants of all types (see pp. 200 and 223).

Sketches of the various types of seatings for use in conjunction with vitreosil basins are shown in Figs. 51 and 53. In order to withstand the intense heat of the fire-gases in the lower portion of the flue, the first three or four rows of seatings are made with closed bottoms, followed by a few rows of perforated seatings to permit of a more intimate contact of the fire-gases. These, in turn, are followed by a number of rows of open seatings, to allow of the full effect of the heat of the flue-gases to act on the basins. The top covers are fitted with lifting holes, so that they can be removed readily whenever required. The fume pipes are also constructed of obsidianite.

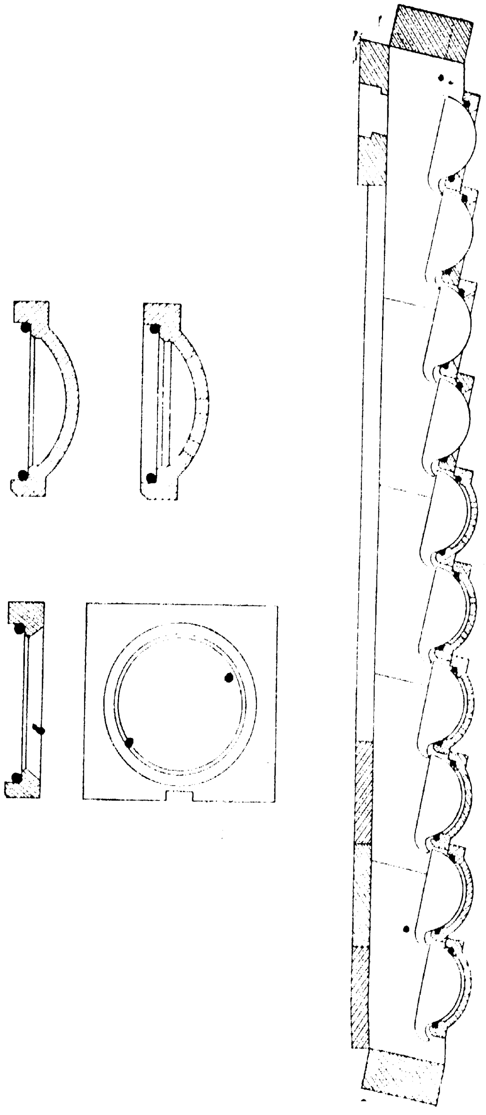

FIG. 53.—Obsidianite Basin Seatings.

Acid-Resisting Iron.

Within the last twenty years ferrosilicon has become a very important material for the production of acid-proof vessels of all kinds, and is now employed extensively in the concentration of sulphuric acid.

In 1900, A. Jouve of Paris, whilst engaged in the analysis of samples of ferrosilicon, noticed that, with certain percentages of silicon, the material was unattacked by acids; thereupon he commenced research work on the preparation of acid-resisting metals, and in 1903 took out a patent covering the use of ferrosilicon alloys[1] (Fr. P. 330666). In 1907, Jouve announced that he had overcome most of the difficulties of manufacture, and commenced to produce vessels made of an acid-resisting material, to which he gave the name "métillure."

According to Hoffmann,[2] this alloy resists the attack of all acids except hydrofluoric acid.

In Germany the so-called "neutraleisen" has been put on the market by Krupp and other firms; and in Italy Rossi has developed the use of ferrosilicon alloys under the name of "elianite" for the concentration of synthetic nitric acid. In England these alloys are sold under the names of tantiron, ironac, and narki metal, and as duriron in America.

The corrosion of ferrosilicon alloys has been studied by Kowalke in America.[3] But it is to be regretted that these experiments were carried out at ordinary temperatures, and not at the boiling-points of the various acids. The figures for a 10 per cent. solution of sulphuric acid are given on p. 119.

These figures show that an alloy with less than 12 per cent. of silicon does not offer a satisfactory resistance to corrosion. Between 12 per cent. and 13 per cent. the speed of attack falls very rapidly, and reaches a minimum between 16 to 18 per cent.; but above 19 per cent. it tends to increase again.

According to Jouve,[4] the composition of "métillure" varies from 15 to 20 per cent. of silicon. A sample with 20 per cent. silicon, when heated for two months with 36° Tw. sulphuric acid, lost only 0·06 per cent. by weight.

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[1] *J. Soc. Chem. Ind.*, 1903, p. 1086.

[2] *Chem. Ind.*, 1911, p. 241.

[3] *Amer. Electro Soc.*, 1917, p. 206.

[4] *J. Iron and Steel Inst.*, No. 3, 1908; Faraday Society, 23rd June 1908.

Si.	Area in sq. cm.	Percentage of loss after				
		51 hours.	75 hours.	141 hours.	22 days.	29 days.
2·5	15·7	1·6	4·1	6·5	...	...
3·3	21·9	64·9	87·5	92·8	...	...
7·4	11·5	31·0	48·9	62·0	...	...
9·9	12·7	10·7	19·8	23·1	...	...
11·1	13·0	5·0	8·8	13·1	42·5	73·1
12·4	9·2	1·2	2·1	2·4	4·6	14·2
13·6	16·6	0·2	0·60	0·90	2·0	3·4
14·8	18·0	0·03	0·05	0·05	0·05	0·05
16·1	10·2	0·03	0·04	0·04	0·04	0·04
17·3	11·9	0·03	0·03	0·03	0·03	0·03
19·8	9·6	0·13	0·20	0·25	0·60	0·70

The equilibrium curve between the solid and liquid phases in these alloys has been studied by Guertler and Tammann[1] who have shown that from 0 to 20 per cent. silicon, the mixture is constituted by mixed crystals of iron and silicide of iron Fe_2Si (Fe_2Si = 20 per cent. Si). They have also studied the fusion of these alloys; but for more recent data see, Sanfourche.[2]

According to S. J. Tungay,[3] in addition to the serious difficulties presented by the considerable shrinkage of these non-corrosive iron castings during cooling, which amounts to $\frac{9}{32}$ in. per foot in each direction, as compared with about $\frac{3}{32}$ in. in the case of ordinary cast iron, the presence of "graphite" in any considerable quantity causes disaster. The carbon and phosphorus content of the iron must also be low, otherwise, during the process of cooling, these compounds may tend to separate out and form eutectics, the separated compounds resulting in pellets, which are found in small blow-holes or cavities in the thickness of the metal. No satisfactory results were obtained until the adoption of the electric furnace for large scale production. By means of suitable furnaces and by improved manipulation in mixing the metal, these difficulties have been overcome largely, and it is possible now to produce an excellent acid-resisting iron on a commercial scale. Tungay gives the following physical constants for acid-resisting iron, as compared with cast iron; but some doubt has been thrown on this comparison.[1]

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[1] *Z. anorg. Chem.* (*Trans.*), **47**, 163; *Rev. Met.* (*Trans.*), 1908, **5**, 550.

[2] *Rev. Met.*, 1919, **16**, 217-224; *J. Soc. Chem. Ind.* (*Abstr.*), 1919, p. 775.

[3] *J. Soc. Chem. Ind.* (*Trans.*), 1918, p. 87.

	Cast Iron.	Acid-resisting Iron.
Density	7·3	6·8
Tensile strength (tons per sq. in.) .	9-10	6-7
Melting-point	1150° C.	1200° C.
Hardness	24	35
Heat conductivity	10	8
Electrical resistance	8	10
Contraction per foot in casting . .	3/32	9/32
Crushing strength	40 tons	34 tons

The heat-transmitting power of acid-resisting iron has been calculated to be nearly ten times the heat conductivity of stoneware or quartz, and about twice that of lead. A serious drawback to the utilisation of these alloys is the fact that they are very brittle, and so extremely hard that it is impossible to machine them, except by grinding with high-speed abrasive wheels. An interesting account of the historical development of the ferrosilicon alloys and a study of their acid-resisting properties is given by Matignon.[2] The analyses of various alloys produced in various countries in 1913 are given, together with some more recent analyses.

	Métillure (France).	Elianite I (Italy).	Elianite II	Ironac (England).	Duriron (America).	Super-neutral (France).
Si . .	16·92	15·07	15·13	13·16	15·51	14·56
Fe . .	81·05	82·40	80·87	83·99	82·23	82·94
Mn . .	0·88	0·60	0·53	0·77	0·66	0·74
Ni . .	...	...	2·23	...	...	...
Al . .	0·25	...	...	...	...	...
C . .	0·592	...	0·82	1·08	0·83	1·20
P . .	0·173	...	0·06	0·78	0·57	0·05
S . .	0·01	...	0·03	0·05	0·01	0·08
Sp. gr. .	6·71	6·87	7·14	6·71	6·94	...

The introduction of 2 per cent. Ni in Elianite II improved the resistance to acid. Analyses were carried out in 1913; since that date the composition of ironac has been improved by reducing the carbon content and increasing the percentage of silicon.

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[1] Hinchley, *J. Soc. Chem. Ind.* (*Trans.*), 1918, p. 91.

[2] *Chem. Ind.*, 1919, pp. 1283-1302.

Sutor[1] gives the following analyses for tantiron and duriron:—

	Tantiron.	Duriron.
Si . . .	14 to 15	14 to 15
Mn . . .	2·00 „ 2·5	25 „ 0·35
C . . .	0·75 „ 1·25 (graphite)	0·20 „ 0·60 (total)
P . . .	0·05 „ 0·10	0·16 „ 0·20
S . . .	0·05 „ 0·15	0·05

The duriron contains less graphite, and hence its mechanical properties should prove superior to tantiron.

G. Varley (in a private communication to the author, July 1921) gives an analysis of narki metal, as follows:—

Silicon	14 per cent.
Carbon	1 „
Sulphur	0·032 „
Phosphorus	0·044 „

Borchers and Monnartz (Ger. P. 246035) describe an acid-proof alloy of chromium-iron containing 10 per cent. chromium and no carbon, with 2 to 5 per cent. molybdenum.

W. & R. Borchers (Ger. Ps. 265076, 265328, 278902, 278908) prepare excellent alloys capable of being mechanically worked, from nickel, cobalt, tungsten, molybdenum, and the metals of the platinum group.

Grimshaw[2] prepares very strongly-acid-resisting alloys by first alloying 40 parts cobalt with 60 parts tin, and dissolving a sufficient quantity of this in copper to obtain alloys of 80 to 95 parts copper with 20 to 25 parts cobalt tin.

Rossi[3] (B. P. 121730, 13th December 1918) prepares alloys containing 13 to 15 per cent. silicon for ensuring resistance to chlorine and to nitric, sulphuric, and acetic acids; or 20 to 21 per cent. silicon for ensuring resistance by hydrochloric acid, by means of the electric furnace, and removes impurities by crystallisation by cooling to not below 1400°. The strength of the alloy is improved by the addition of small proportions of fluxes—such as iron sulphate.

Kowalke[4] prepares copper aluminium-iron bronzes with satisfactory mechanical properties, which are resistant to acids. An alloy having the composition Cu 87 per cent., Al 9·8 per cent., "iron alloy" 3·1 per cent., is particularly resistant to sulphuric, phosphoric, tartaric, and acetic acids; but is attacked by hydrochloric acid and ammonia, and at a very rapid rate by nitric acid.

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[1] *Stahl u. Eisen*, 1917, p. 309.

[2] *Chem. Eng.*, **17**, No. 2; *Chem. News*, 1913, p. 283.

[3] *J. Soc. Chem. Ind.* (*Abstr.*), 1920, p. 787.

[4] *Chem. and Met. Eng.*, 1920, **22**, 37-38; *J. Soc. Chem. Ind.* (*Abstr.*), 920, p. 158.

Parr[1] (U.S. P. 1115239) describes a chromium nickel copper alloy called "illium" as a substitute for gold or platinum. The alloys withstand hot or cold, strong or dilute, acids, and can be cast and machined.

Clement[2] (U.S. P. 1333706, 16th March 1920) describes an acid-resisting alloy containing Cr 60 Fe 39·2 to 39·7 and C 0·3 to 0·8 per cent., the carbon being present as a carbide of chromium and iron.

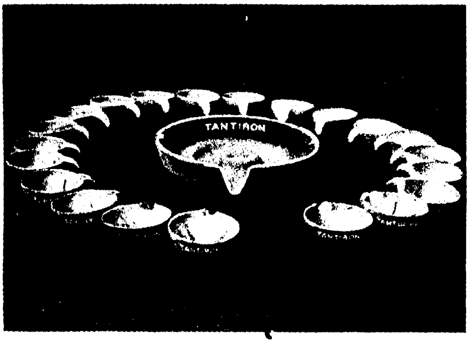

FIG. 54.

Irmann[3] describes the preparation of nickel copper alloys resistant to sulphuric acid. The maximum resistance is found in the 50 per cent. alloy.

Tantiron is manufactured by the Lennox Foundry Co., Ltd., at Glenville Grove, New Cross, London, S.E., as a hard, close-grained alloy, melting at about 1200°; not rusting, not oxidising, and not attacked sensibly by the ordinary corrosive substances. Castings varying from a few ounces up to many tons in weight can be made of it, and it has been used extensively for many purposes throughout the chemical industry, and especially in the concentration of sulphuric acid. Fig. 54 shows the types of evaporating basin used. The use of the larger vessel is recommended by the makers, according to whom twenty-one 12-in. basins evaporate the same quantity of acid as one 36-in. corrugated pan, and both expose the same heating surface (7 sq. ft.) to the fire-gases.

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[1] *J. Soc. Chem. Ind.*, 1914, **33**, 1161; 1915, **34**, 1097; *Mining Journal*, 27th December 1919.

[2] *J. Soc. Chem. Ind.* (*Abstr.*), 1920, p. 520.

[3] *Metall. u. Erz.*, 1917, pp. 21-30, 37-42; *Z. angew. Chem.*, 1917, Ref. 210; *J. Soc. Chem. Ind.*, 1917, p. 928.

	For 21 Small Basins.	For 1 36-in. Pan.
The surface exposed to corrosive action is	3969 sq. in.	1374 sq. in.
The total acid in circulation	478 lb.	221 lb.
The total weight of basins	210 lb.	196 lb.

Per ton of acid concentrated, the large pans take 20 per cent. less fuel, and require less labour.

Owing to the low tensile strength of ferrosilicon alloys, it has been found impossible to make bolts, nuts, or screws, etc., to replace those made of steel; but Messrs Lennox Foundry Co., Ltd., have succeeded in producing a "Tant-Copper" alloy, which, while it is equally resistant to attack from all ordinary acids as ferrosilicon alloys, is as easily machined as bronze, and has a high tensile strength.

Narki metal is manufactured by Messrs John Varley & Co., Ltd., Waterloo Foundry, St Helens. Although of more recent date than the other ferrosilicon alloys, narki metal has succeeded in obtaining a very wide application in the chemical industry, as it has the distinctive property that all flanges and joints can be machined in the lathe. The qualities demanded of a satisfactory acid-resisting material are many and various. In addition to its acid-resisting properties, it must have sufficient strength, tensile and transverse, to withstand rough usage, and must be proof against cracking under sudden changes of temperature. It must be capable of being machined in the lathe, and of withstanding the strain to which it is subjected when the bolts are tightened at the joints. At the same time it must be of such a nature that it can be cast into vessels of the desired sizes and shapes. In short, it must possess as nearly as possible the mechanical properties of cast iron, with the additional quality of acid resistance approximating to that of porcelain and other fragile material of a similar nature. It is claimed by the makers that all these demands have been met by "narki" metal.

One use to which "narki" metal has been applied with good success is in connection with the cascade system of concentrating plant. The usual size of the basin is 12 in. diameter by 6 in. deep; but the larger size, 36 in. diameter by 7½ in. deep, is also used extensively, and gives a much larger output (see Figs. 55-58).

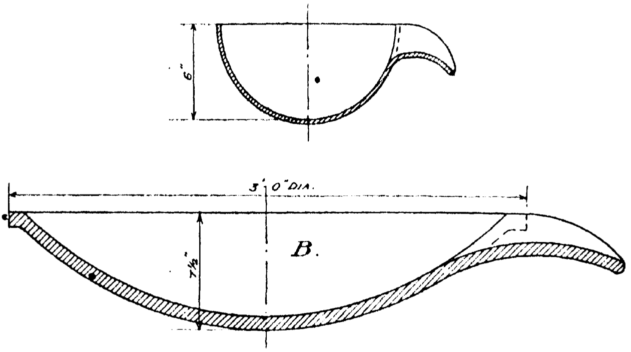

FIG. 55.—"Narki" Metal Basins.

Ironac is manufactured by Haughton's Patent Metallic Packing Co., Ltd., 30 St Mary-at-Hill, London, E.C., and has had a wide application in all types of sulphuric acid concentrating plant, but especially in the cascade rectifying plant (see p. 136).

Hartmann and Benker[1] describe a cascade plant in which the porcelain dishes (see p. 102) are replaced by special acid-resisting iron vessels made by the A. G. fur Bergbau und Eisenhuttenbetrieb at Kattowitz (Silesia)—see p. 118. The eight lead pans employed for the preliminary concentration are arranged in two sets of four each, heated by the waste fire-gases of the cascades. The pans are made of a special acid-resisting

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[1] *Z. angew. Chem.*, 1909, pp. 395-97.

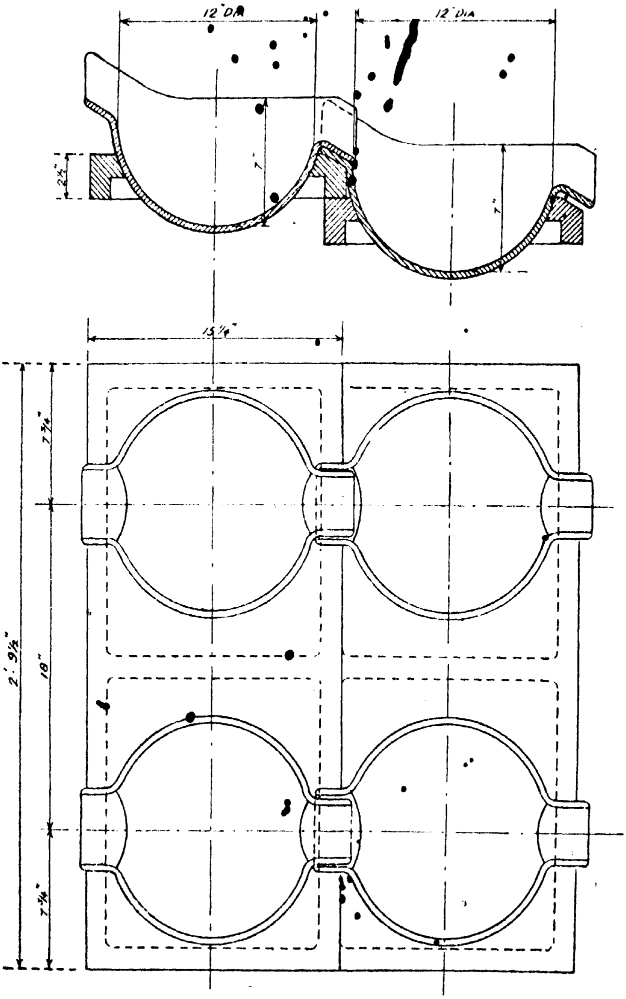

FIG. 56.—Double-lipped "Narki" Metal Basins with Cast-iron Seats.

description of lead ("krellblei"), in which the acid can be brought up to 152° to 155° Tw. without any considerable wear and tear. In a private communication to the author (June 1921) Messrs Benker and Millberg state that they add about 0·2 per cent. of copper to the lead used for the lead pans. The "neutraleisen" dishes are 320 mm. wide at the top, and 165 mm. deep, and are placed on fire-clay rings, in two parallel rows arranged in cascade form, and heated directly by the fire-gases from an ordinary coke-gas producer. Fused silica dishes (see p. 108) have also been used, with good success, and have replaced the "neutraleisen" dishes to a large extent. For a detailed description of this plant, as erected in 1911, see our fourth edition, pp. 1176-1178.

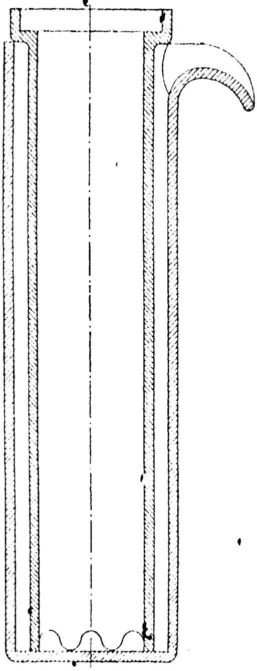

FIG. 57.—"Narki" Metal Cooler.

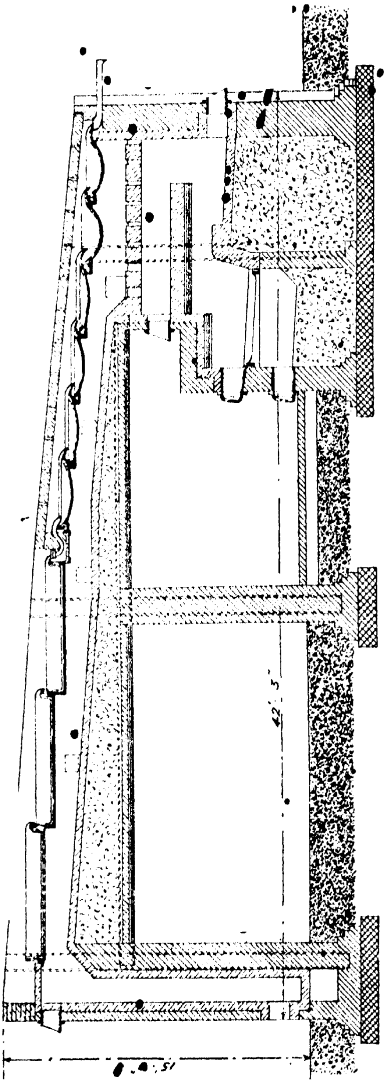

FIG. 58.—Cascade Concentrator with 3 ft. diameter "Narki" Metal Basins.

Mackenzie[1] (B. P. 2389 of 1912; B. P. 6415 of 1909) constructs a cascade plant, using vessels of the shape shown in Fig. 59.

W. Mason[2] describes a "capsule" plant comprising six lead pans and forty fused silica basins, in which 4 tons of 95¼ per cent. H_2SO_4 were produced from 65 per cent. feed acid per twenty-four hours, at a cost of 6s. 4½d. per ton. The exit gases take only 2·23 per cent. of the acid away, as against 15 per cent. in the glass retort system. With a forced draught furnace, too high a temperature is produced in the lower part of the plant, causing bumping and breaking.

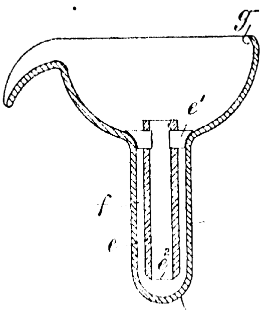

FIG 59.

A. Marshall[3] states that the breakages in fifteen factories are under 5 per cent. per annum, from all causes, and the fuel consumption 17 per cent. of the weight of finished acid.

F. Brown and the United Alkali Co., Ltd., Liverpool (B. P. 183, 9th October 1916), describe an improved form of basin with two spouts. The inlet spout of each basin rests on the edge of the support of the basin next above, and the outlet spout rests in the inlet spout of the basin next below.

Moss[4] states that the fuel consumption on a continuous cascade plant of stepped basins is about 25 per cent. of the weight of concentrated acid produced. Gas firing is preferable, as it can be regulated easily, and the working of the plant is not upset by the cleaning of the fire. The maintenance of cascade plants is heavy, as the breakages of basins means that the hot acid falls into the brickwork of the flues below. These tend to get distorted in time, and cold air is drawn in, with loss of efficiency. The impurities (chiefly iron) contained in the acid are deposited in the basins in the form of crusts, which tend to cause the acid to bump, and ultimately crack the basin.

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[1] *Chem. Trade J.*, 1912, p. 459.

[2] *Met. and Chem. Eng.*, 1915, p. 17; *J. Soc. Chem. Ind.* (*Abstr.*), 1915, **34**, 135.

[3] *Ibid.*, p. 136; *J. Soc. Chem. Ind.*, 1915, p. 350.

[4] *J. Soc. Chem. Ind.* (*Trans.*), 1918, p. 68.

C. Stoffmehl (Fr. P. 460527; Belg. P. 258323 of 1913) concentrates sulphuric acid in a set of fused silica dishes, placed partly inside, and partly outside, of a tower made of acid-proof material, in such a manner that they are heated consecutively by the fire-gases. The dishes placed inside the tower are fed with the acid previously concentrated in the dishes outside the tower.

W. K. Lewis[1] describes experiments of the heat-transmitting capacity of fused silica dishes. Solutions of boiling-points ranging from 100° C. (water) to 240° C. (zinc chloride) were evaporated in a silica dish set in an ordinary gas crucible furnace, and the heat consumption calculated from the quantity of water required to keep the volume of solution constant during evaporation.

In the concentration of sulphuric acid in silica dishes, it is recommended that a thick fuel bed be used with insufficient air for complete combustion, and with injection of steam, if necessary further to reduce the temperature to which the dishes set directly over the fire are exposed. The carbon monoxide or water-gas produced is burned by introducing air along the flue, which is packed with heat-conducting refractory material to facilitate radiation. In this way breakages are minimised, and a very regular temperature maintained along the flue.

Carmichael and Guillaume[2] (B. P. 15678 of 7th July 1913) describe an improved form of basin fitted with a deflector (see Fig. 60), which is detachable from the basin, and consists of a half tube of semi-circular cross-section, curved so as to lie with its edges against the sides of the basin, from nearly the bottom up to, and beyond, and overhanging the lip of the vessel. In ordinary practice, without a deflector, the acid from the basin above flows on to the surface of the one next below it; passes across the surface and over the lip of the basin. In this way the bulk of acid is not properly displaced, and gives rise to an accumulation of iron salts, which are very difficult to remove, and increase the difficulties of working the plant. The deflector

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[1] *J. Ind. Eng. Chem.*, 1915, pp. 410-14; *J. Soc. Chem. Ind.*, 1915, p. 600.

[2] *J. Soc. Chem. Ind.*, 1914, p. 919.

compels the dense acid from the bottom of the basin to be forced over the overflow to the next below it in the cascade, and thus disturbs any deposit of iron salts, which are therefore kept in movement, and descend through the cascade into the cooler at the lower end whence the iron salts may be removed

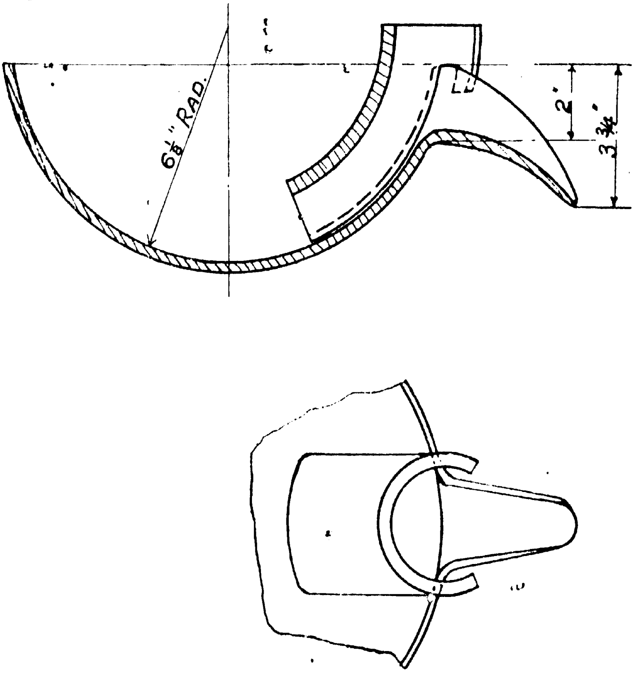

FIG. 60.

easily. The device may be made in fused silica or any acid-resisting ware.

According to information supplied by Messrs Benker & Millberg (May 1921), the French manufacturers employ almost exclusively the Kessler and Gaillard systems of concentration (see pp. 168 and 195), and use the cascade system only when a quite pure water white acid is required. The present arrangement of the plant is shown in Fig. 62.

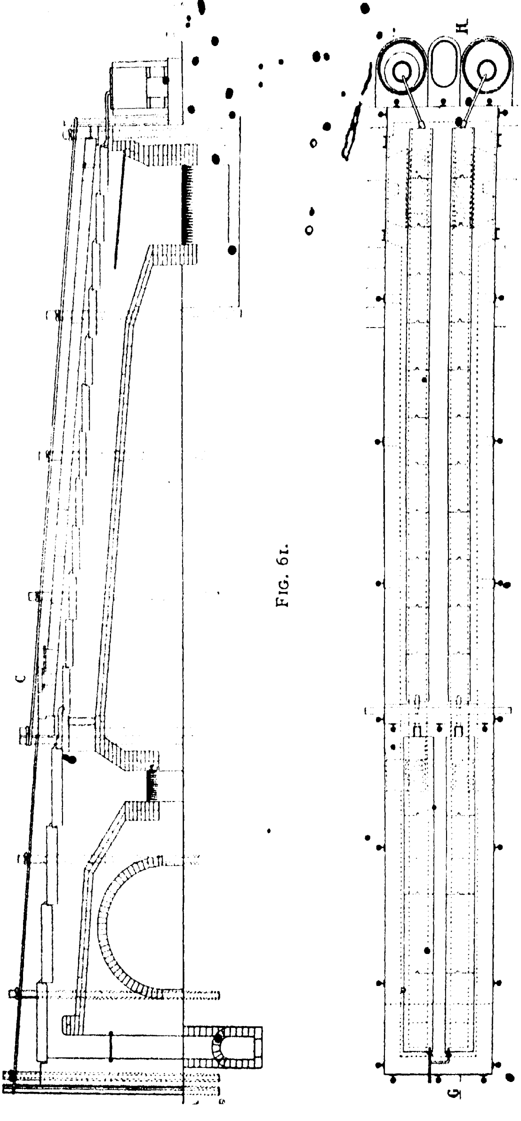

Fig. 61.

Two parallel rows of rectangular quartz dishes are arranged in cascade form, so that the acid overflows from the lip of each upper pan and runs into the next lower one. No fireclay supports are used, and the dishes rest on the sides of the fire flue, and are directly exposed to the heat of the gases. In the drawing, an ordinary type of fire-grate is shown, together with a small subsidiary grate for heating the preheaters, but a small coke gas-producer is preferable. The first four quartz vessels (1000 mm. × 400 mm. × 150 mm.) serve to preheat the acid, and are uncovered, as no fumes are evolved at this stage of the process. The concentration proper is carried out in twelve quartz vessels (610 mm. × 310 mm. × 100 mm.) enclosed in a volvic chamber, from which the vapours are drawn off by means of a Kestner fan, and pass, first through a cooler, and then through a coke scrubber to remove the traces of acid mist. The acid condensed in the scrubber varies in strength from 35 to 65° Tw., and is run back again into the feed acid. The concentrated acid leaves the plant at strength of 168° Tw.; as it comes in contact with quartz only during its passage through the plant, it is as clear as water and free from impurities.

Leitch (B. Ps. 1495 and 16001 of 1915; U.S. Ps. 1257894, 1257895 of 1915) concentrates sulphuric acid in a continuous cascade in three stages; first in lead pans up to 75 to 80 per cent H_2SO_4; then in intermediate vessels up to 85 to 90 per cent.; and finally up to 96 to 98 per cent. in iron pans, separately enclosed in a muffle type of furnace under and over which the hot gases are circulated. The vessels intermediate between the lead pans, which are preferably open, and the iron pans, which are separately enclosed, may be of silica, glass, porcelain, or any acid-resisting alloy capable of withstanding acid of this strength. These vessels are enclosed in order to recover the dilute acid carried away by the vapour. At a suitable level above the uppermost of the lead pans, reservoirs are placed for the weak acid to be concentrated, from which the acid flows down towers which preheat the acid before it is fed to the lead pans. The iron pan in which the final concentration takes place is closed by a suitable cover, so that the hot vapours arising from the pan are collected and led to the towers, which are placed more or less directly over

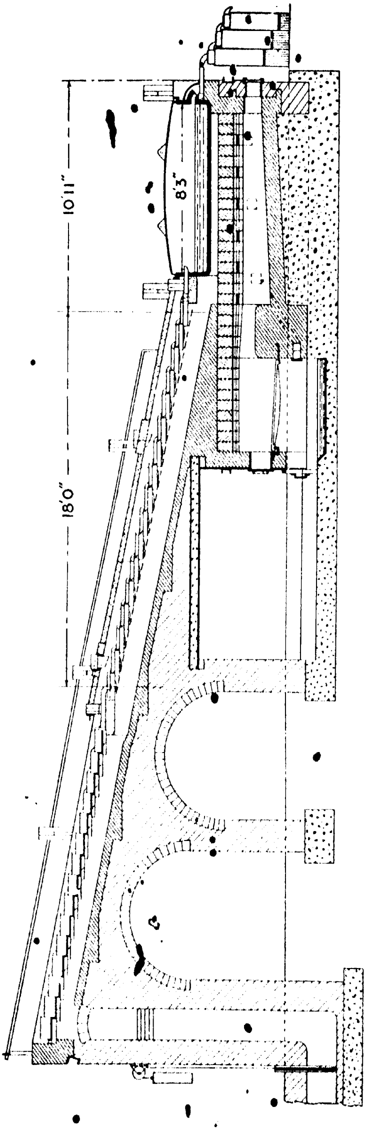

FIG. 65.

cent. H_2SO_4) is required. An increase in the output of the plant is obtained also, so that the greater flow of acid through the basins tends to reduce the formation of deposits, and, in consequence, to reduce the number of breakages and the time spent in cleaning operations. Irregularities in the life of the iron pans are very frequent, and may be attributed to (1) variation in the material of which the pan is made; (2) irregular firing of the furnaces (this does not occur with gas or oil firing to the same extent as with coal firing); (3) occasional carelessness in running down the acid too weak into the pans, thus throwing too much work upon them, in addition to causing corrosion. (One disadvantage of the use of iron pans at the bottom of the cascade plant is the fact that, in the event of the plant standing idle at any time, the surface acid absorbs moisture from the air and causes corrosion at the liquid air line, owing to the formation of weak acid.)

Fig. 65 shows the general arrangement of a typical standard cascade plant, fitted with an iron pan at the bottom for bringing the acid up to 96 per cent. H_2SO_4. The acid level in the pan is maintained at about 6 in. depth, to prevent silting up with iron sulphate, which reduces the efficiency of the plant. The pan is fitted with a separate fume pipe of lead-covered earthenware, or, preferably, of a ferrosilicon alloy, and the vapours are condensed separately. The condensed acid flows through a Twaddell jar, and the strength furnishes a sound guide to the working of the plant, so that the firing and flow of acid can be regulated to obtain a continuous run of high-strength acid.

Fig. 66 shows the type of cast-iron pan and cover supplied by Messrs John Varley & Co., Ltd., of St Helens, Lanc., for the concentration of sulphuric acid. The internal dimensions of the pan are 7 ft. 2½ in. long by 2 ft. 11½ in. wide by 17½ in. deep, and 4 in. thick, with an inlet and an outlet for the acid, and an outlet on the cover for the fumes. Such pans are employed very extensively for the final concentration of sulphuric acid in cascade plants.

According to the *Alkali Inspector's Report for* 1915 (p. 73), the advantages derived from the introduction of cast-iron pans into the bottom of a cascade plant are two-fold. In the first place, an increased production of acid is obtained; secondly, the greater flow of acid through the basins tends to retard sedimentation, and there are fewer breakages in consequence, and less loss of time spent in cleaning operations.

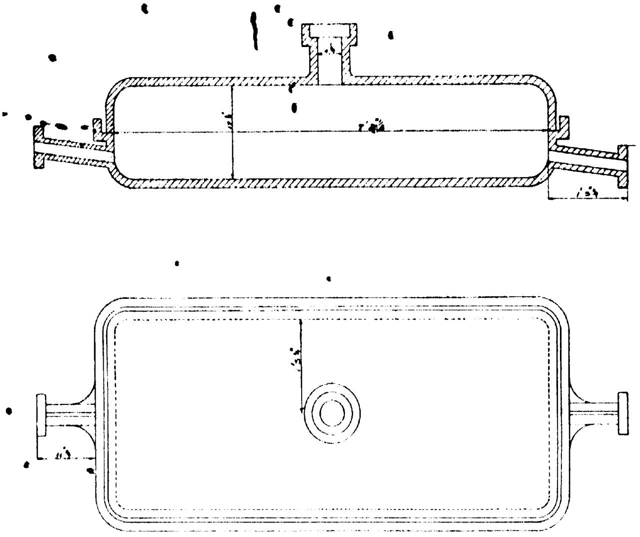

Fig. 66.

Ironac Cascade Plant.

An ironac cascade concentrator (Fig. 67) illustrates the Haughton-Tungay system of improved cascade concentrator as constructed in ironac (B. P. 114072 of 23rd May 1917[1]). This is a modification of the cascade system, consisting of a series of rectangular preheating trays made of ironac metal, for the gradual heating up of the cold acid to be concentrated. The run-off from the trays is arranged alternately right and left-hand, to increase the travel of the acid, and hence the time of contact with the flue-gases; the trays are not covered, as no fumes are evolved in this portion of the plant. The acid from the trays passes through a connecting-pipe into a run of small ironac basins of semi-spherical shape, each 300 mm. diameter by 150 mm. deep, and having an outlet lip. The upper edges of the

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 266A.

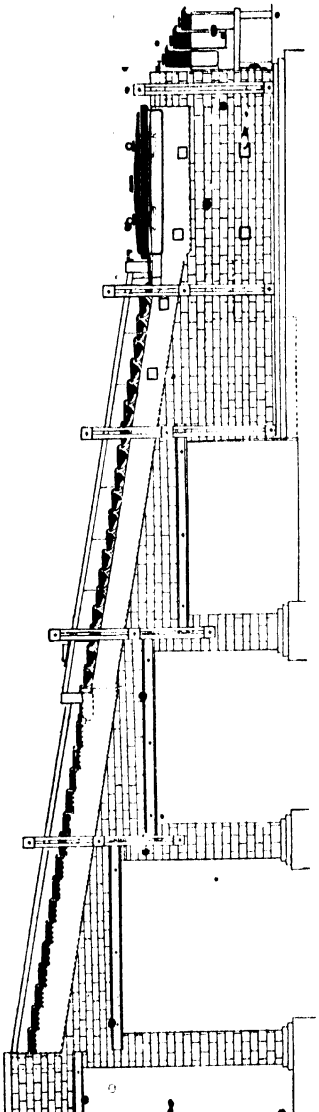

FIG. 67.

basins are corrugated to facilitate the free expansion and contraction of the metal, and also to prevent any loss through the frothing of the acids during concentration.

Fig. 67A shows an improved basin, fitted with a baffle placed around the outlet, so that only the strong acid from the bottom portion of the basin is allowed to escape. A fume flue is formed over the basins by means of acid-proof slabs, and the fumes evolved during the concentration process are drawn away to suitable condensers.

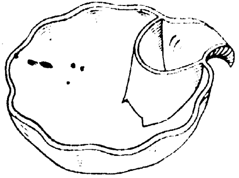

FIG. 67A.

With a view to reducing floor space and obtaining higher efficiency, a visible type of cascade plant has been designed, and a number of installations are working with considerable success (Fig. 68). The main feature of the plant consists of twelve shallow ironac pans, each 3 ft. diameter, and each having a separate cover, fitted with a fume pipe leading to a common flue for conveying the fumes to a scrubber. In this way the plant is open practically always to view, and temperatures can be taken from each of the pans regularly. It is claimed that much less floor space is occupied by this system, and a higher efficiency obtained. Dealing with cold sulphuric acid of 64 to 65 per cent., and concentrating up to 93 to 94 per cent., this plant will produce 10 tons per twenty-four hours of finished acid, with a fuel consumption of 12 per cent. of the weight of acid produced, according to information supplied by the makers.

A further modification of the cascade system by Tungay consists of a series of corrugated trays or plates, over which the acid in course of concentration slowly ripples throughout the length of the plant. The trays are set in special fire-brick settings over inclined flues, to allow of gravitation of the acid whilst in the course of concentration. The noticeable feature with this plant is that very little weight of acid is contained in the plant during the actual period of treatment; whereas, with the system described above, a very considerable quantity of acid is retained always in the plant itself; this fact always presents a certain amount of difficulty whenever breakage or the necessity of replacing a vessel occurs. This rippling cascade type is said to be a very efficient design.

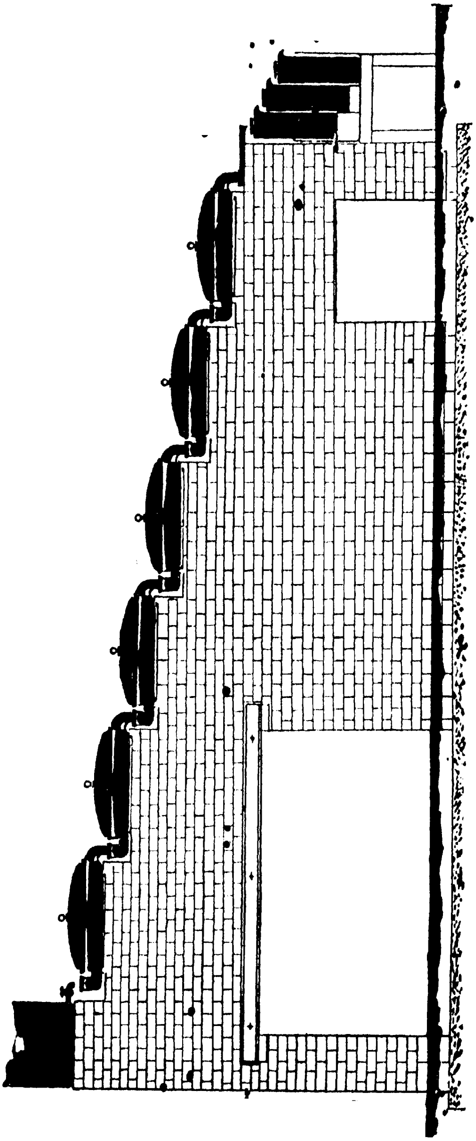

FIG. 68.

According to the 51st *Alkali Inspector's Report for* 1914, the use of the cascade system for the concentration of sulphuric acid was extended during the year. 'It is important to maintain a proper relation between the draught in the fire-flue and that in the fume flue. In several cases an undue escape of acid vapours was caused by the fact that the draught in the fire-flue was stronger than in the other flue, so that the fumes went into the chimney instead of going into the condenser.

The following remarks on the cascade system are made in the 52*nd Alkali Inspector's Report for* 1915:—

For the efficient and satisfactory operation of the cascade type of concentrating plant, it is essential that: (1) a greater draught should be given to the flue leading the evaporated gases and vapours towards the condensers than is given to the fire-flue leading the fire-gases to the chimney; (2) excessive local intense heating of any section of the cascade be avoided; (3) adequate means for the condensation of the acid vapours be provided.

Sufficient draught on the fume flue ensures the proper removal of vapours of evaporation; it thus increases the amount of work done by the plant, and at the same time prevents the objectionable acid fumes from being drawn into the fire-flue, to pass thence by way of the chimney into the air. Intense local heating leads to badly balanced evaporation; to dissociation of the acid, with a consequent undue formation of fume; to violent ebullition in some of the vessels, leading to breakages, entailing further formation of fume accompanied by general deterioration of the plant. Adequate condensers are necessary, in the interests of the public, and are practicable on all such plants. From experience gained in the past, the tables on pp. 141, 142 have been compiled for the information of those who have to do with the erection and operation of these plants.

According to the *Alkali Inspector's Report for* 1915 (p. 93), experiments made in covering over with sheets of asbestorite the open silica pans usually installed in one type of cascade plant have shown a considerable increase in the temperature and strength of acid, as compared with the preheaters exposed to air currents. The actual mean figures were:—

Exposed: strength of acid entering and leaving preheaters 116° and 118° Tw.
Covered: „ „ „ 116° „ 124° „

Difference 6° Tw.

Basins of Silica, Ironac, Narki, and Tantiron, with Preheaters.

Acid Feed Strength.	Number of Basins.	Output Tons Acid per 24 Hours. 166-169° Tw.	Water and Acid evaporated per 24 Hours. Tons per 100 Basins.			Packing in Condenser.			
			Loss of Strong Acid assumed to be—			Per Basin.		Per Ton, Strong Acid made.	
			Nil.	5 %.	15 %.	Volume cub. ft.	Sectional Area sq. ft.	Volume cub. ft.	Sectional Area sq. ft.
						Coke packing			
105° Tw.	727	61·5 = 1·69 cwt. per basin	4·5	5·1	6·4	6·5	1·6	77	18
123° Tw.	1440	112 = 1·55 ,,	3·1	3·6	4·7	8·2	0·7	105	10
136° Tw.	40	4 = 2·0 ,,	2·7	3·3	4·6	6·2	1·2	62	12
147° Tw.	100	15 = 3·0 ,,	2·9	3·8	5·5	7·5	...	50	...
						Ring packing			
120° Tw.	40	2·5 = 1·25 ,,	2·5	2·9	3·8	5·0	...	76	...

Cascade Plant and Condensers with Preheaters.

Acid Feed Strength.	Description of Plant.	Output of Acid.		Packing in Condenser.				
					Per Basin.		Per Ton Strong Acid made	
		Tons per 24 hours.	Strength Tw.	Nature.	Volume cub. ft.	Sectional Area sq. ft.	Volume cub. ft.	Sectional Area sq. ft.
110° Tw.	3 tantiron pans and basins . . .	5	168	Coke . .	...	...	43	7
125° Tw.	12 tantiron dishes (3 ft. dia.). . .	12	166	Bricks and tiles	...	...	33	...
126° Tw.	80 silica basins and 2 iron pots (8 ft. × 3 ft.)	14	168	Rings . .	...	...	15	...
135° Tw.	Webb plant (30 vessels) . . .	4·5 (3 cwt. per vessel)	168	Coke and brick	14·5	15·1	96	101

These figures represent actual practice, and should not be taken as affording a standard of excellence, as in many cases experience has shown that increased condenser space has been found necessary (*Alkali Inspector's Report*, 1915).

The 53*rd Alkali Inspector's Report for* 1916 contains the following remarks on the cascade plant.

Of the various types of concentrating plant the "Cascade" system was the most numerous, and the most varied in design. This type lends itself more readily than others in use to undue escape of fume through faulty design and construction, or through over pressure in production.

The high acidity of exit-gases may be traced to one or more of three causes: (1) excessive boiling in the lower basins, due in some instances to bad constructional details; in others to an attempt to over-drive the plant; this excessive boiling, especially when there is a deposit of iron sulphate in the basins, causes ejection of acid, and even breaking the basins, with the result that the acid finds its way into the fire-flue; (2) insufficient size of scrubbers employed for dealing with the exit-gases for the plant; (3) insufficient draught on the basin flue, so that a portion of the gases passes downwards into the fire-flue instead of going to the scrubber.

The 54*th Alkali Inspector's Report for* 1917, refers to the advantages of careful firing in cascade plants, and mentions one large installation where coal firing by means of mechanical stoking gave excellent results, due to equable heating and the minimising of temperature fluctuations so detrimental to the basins, and which is due to intermittent admission of excess of cold air.

According to *Bulletin* 184 *of the Bureau of Mines* (p. 135), since the development of fused silica basins there has been a more general adoption of the cascade system of concentration in America, and several plants have been erected. The largest is at the Davison Chemical Co. at Baltimore, Md.

January-June 1918.

Factory.	Production. Tons H_2SO_4.	Loss.	Efficiency.
Craigleith	4,405·9	8·3	91·7
Litherland (Jan.-May)	6,737·0	9·1	90·9
Oldbury (Jan.-Feb.)	1,128·0	5·0	95·0
Penrhyndeudraeth	2,510·9	8·9	91·1
Pembrey (Jan.-April)	1,640·3	12·4	87·6
Queensferry (Jan.-Feb.)	511·3	9·6	90·4
Average	16,933·4	8·9	91·1

The figures on preceding page on the efficiencies of cascade concentrators have been abstracted from the *Second Report on Costs and Efficiencies for H.M. Factories*, issued by the Department of Explosives Supply, Ministry of Munitions (p. 63).

Concentration in Iron Vessels.

The behaviour of cast (and wrought) iron against sulphuric acid has been described in Vol. I., p. 239 *et seq.*

Above 93 per cent. strength there is very little action on cast-iron, and hence cast-iron pans are used frequently for concentrating sulphuric acid from 92 to 93 per cent., to 96, or even 98 per cent. H_2SO_4. In some places they employ long pans (about 10 ft. by 2 ft. deep) covered with a leaden dome, in which the acid (not below 96 per cent.) is heated to 240° C. At one end a stream of heated air is blown in; at the other end the acid vapours escape by a lead tube into a lead condenser. The constant change of air allows of bringing the strength up to 98·5 per cent. At the end of the operation, when drawing off the concentrated acid, enough is left to yield acid of not less than 96 per cent. when feeding with ordinary acid of 93 to 94 per cent. In other places they employ pans with rounded corners, of 6 ft. 6 in. by 3 ft. 3 in. by 1 ft. depth, provided with three necks (one for feeding, two for the acid vapours). The joints are made good with a mixture of asbestos and silicate of soda solution. Near the bottom there is an outlet pipe for the acid. The pans are surrounded by fire-flues, which keep even the covers hot. Two such pans, placed terrace-wise, and weighing about 7 tons, inclusive of connections, are said to produce (from acid of 142° Tw.) 4 tons of 98 per cent. acid per twenty-four hours, with an expenditure of 25 to 27 per cent. of coals.

Tate[1] mentions pots 9 ft. wide, 6 ft. deep, and 2 in. thick, with cast-iron lids weighing 11 or 12 tons, in which acid of sp. gr. 1·74 is concentrated within twenty-eight or thirty hours, to 96 per cent. One such pot produces 12 tons of acid. It is allowed to settle and cool for twelve hours, so that one of these pots can be finished every two days. From time to time the mud, consisting of iron salts, must be cleaned out; and this represents 4 or 5 per cent. of acid lost.

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[1] *J. Soc. Chem. Ind.*, 1894, p. 208.

A detailed account of the types of cast-iron pans employed in America is given by Lunge,[1] and is abstracted fully in the 4th edition of this work, which should be consulted for additional information. As the plants are now obsolete, only a brief description is given below.

In one place they concentrate from 93·5 per cent. to 98 per cent. H_2SO_4 in round cast-iron pans, 3 ft. wide and 2 in. thick, with double flange for a hydraulic joint, in which a water-cooled leaden hood dips. The hydraulic flanges are lined throughout with lead, as they are filled with weak acid; such a pan lasts two months. At another place they have two specially fired iron retorts, with a bottom part 8 ft. by 2 ft. section, and 8 in. deep, connected by a flange and rust-joint with a lid only 4 in. deep. The fire plays all round—first underneath the pan, and then above it, in a 12-in. wide flue. The 6-in. vapour-pipe passes through this. The acid attains 98 per cent. H_2SO_4. When the acid is used only for refining petroleum, the pans are heated by heavy petroleum (sp. gr. 0·833—the residue from the manufacture of paraffin) injected by a steam-jet.

The travel of the acid through the cast-iron pan is increased in the plant erected by W. Quinan, by means of longitudinal partitions, which divide the pan into three channels. The bottom of each channel is bulged outwards in order to enlarge the heating surface. The pans are 5 ft. 6 in. long, 1 ft. 6 in. broad, and 10 in. deep. The channels are 5 in. wide, and the thickness of metal $\frac{5}{8}$ in. The duration of an iron pan is from four to eight months, and chilled cast-iron gives the best results. Small holes sometimes forming at the inlet can be stopped up by silicate of soda cement. A deposit is formed at the bottom consisting principally of iron sulphate, which is removed regularly every fortnight. The pan is emptied, the cover removed, the outlet closed, and the pan filled with water and heated to boiling. The crusts, which are sometimes $\frac{1}{2}$ in. thick, are then chiselled off. Such crusts, of course, greatly diminish the heating efficiency.

The fuel consumption for making 97 per cent. acid is equivalent to 28 to 30 per cent. of coal, but is used in the shape of crude petroleum, sprayed by superheated steam. The introduction of this system in lieu of a coal fire has not merely saved labour, but also increased the output very considerably.

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[1] *Z. angew. Chem.*, 1894, p. 135.

Scheurer-Kestner[1] employs cast-iron pans fitted with a platinum dome.[2]

Hartmann (B. P. 2839 of 1879) saturates the acid with iron salts, which, during the concentration, again separate out and protect the iron of the pan against the acid.

Menzies (B. P. 3230 of 1883) asserts that sulphuric acid of the highest concentration can contain but traces of iron and arsenic in solution, provided the latter be present as arsenic acid, but, according to analyses quoted in the *20th Alkali Inspector's Report* (1883), p. 45, the removal of arsenic is nothing like complete.

In the *28th Alkali Inspector's Report* (p. 55) Graham's process is mentioned, in which the concentration takes place in a series of cast-iron dishes. It was found that hot sulphuric acid in thin layers, in contact with cast-iron, tends to dissociate into SO_3 and H_2O, so that from a certain point the acid becomes weaker, the longer and more strongly it is heated. The dissociation is caused evidently by the superheating of the iron, which becomes much hotter than platinum. This observation proves the advantage of causing the flame to travel in the same direction as the acid, so that the strongest acid is not in contact with the hottest part of the flame. In such dishes the acid cannot very well be brought up higher than 92 to 93 per cent. H_2SO_4; whilst in deeper cast-iron pans, higher strengths can be reached (see p. 144).

Herreshoff, H. and G. Nichols[3] (B. P. 1998 of 1887; U.S. P. 357528) cause sulphuric acid, previously concentrated up to 86 per cent. H_2SO_4, to flow in a zigzag canal, whereby it is exposed to such a degree of heat that it is concentrated up to 95 or 96 per cent. From here it flows into another similarly shaped vessel, heated to such a degree that a half to two-thirds of the acid goes away in the shape of vapour, and is condensed to acid of 93·5 per cent., nearly chemically pure. This process is described by Chandler.[4]

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[1] *Bull. Soc. Ind. Mulhouse*, 1892, pp. 320-348.

[2] See 4th edition, pp. 1165-1166.

[3] *J. Soc. Chem. Ind.* (*Abstr.*), 1887, 6, 370.

[4] *J. Soc. Chem. Ind.*, 1908, p. 269.

MacKenzie's B. P. (26278 of 1904) is described in the *Chem. Trade J.* of 1905, 36, 166. Acid of sp. gr. 1·55 is run from a store-tank through a lead coil, heated by the waste gases from a tower below, filled with bricks, where it is concentrated to sp. gr. 1·775 to 1·800 by direct contact with the hot fire-gases, coming from the cast-iron pot, where the final concentration takes place. Here hot air, produced in a chamber containing cast-iron pipes, is blown through, whilst the pot is heated externally by the gases coming from the air-heating chamber. The temperature in the cast-iron pot need not exceed 270°, since the hot air blown through is sufficient to bring up the acid to full strength at that temperature.

Ellison[1] (B. P. 17760 of 1902) concentrates sulphuric acid in a closed cast-iron pan, within which is a pipe of acid-resisting material, of rather less diameter than the pan, and having its bottom edge serrated. Dilute acid is led into that pipe, and is concentrated by the heat from the surrounding strong acid. As the acid in the inner pipe becomes concentrated, it flows through the serrations to replace the concentrated acid in the pan. A leading object of the invention is, that only concentrated acid shall come in contact with the cast-iron boiler.

Evers[2] (Ger. P. 176369) effects a continuous concentration of acids by means of two coils of pipes interposed between each other, on the bottom of the pan, through which the liquid passes on. The concentrated acid runs out at the side, after having given up part of its heat to dilute acid introduced in the centre of the vessel.

Proelss and Hall[3] (U.S. P. 960702) employ a cast-iron pot or boiler, provided on the top with an annular flange and rim; from this a pipe leads to an extension with interstitial "packing," over which the weak acid flows on its way to the boiler. As the level of the acid boiling in the pot rises above the flange, the strongest acid from the bottom passes out and upwards by a tube into a second pot placed over the first; here the acid is made to travel over the bottom in a thin layer, and is thus highly concentrated. Acid of 98·2 per cent. is said to be produced continuously by this apparatus.

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[1] *J. Soc. Chem. Ind.*, 1903, 22, 950.

[2] *Z. angew. Chem.*, 1907, 20, 1066.

[3] *Chem. Zeit. Rep.*, 1910, 34, 342.

Stange[1] (B. P. 91 of 1907; Ger. P. 188901; U.S. P. 837592; Fr. P. 372326) concentrates sulphuric acid in conical cast-iron pans, the sides of which are heated outside, by means of hot air being blown over the surface of the liquid. The bottom of the pan is cooled, and has a conduit leading to a cooling chamber beneath. In the pan a stoneware vessel with an opening at the bottom is suspended, through which the dilute acid must pass before getting into the cast-iron pans; thus the lighter dilute acid floats on the already concentrated acid, which does not mix with it, as it is prevented from boiling by the cooling of the pan-bottom. Therefore the sludge, inevitably formed when concentrating sulphuric acid in cast-iron vessels, does not burn fast to the bottom, but remains in the form of a mud, which is let out easily at the bottom without stopping up the outlet for the concentrated acid situated higher up. The escaping vapours are condensed in a Glover tower.

Friedrich[2] recommends a cast-iron concentrating apparatus in which acid of 106 or 142° Tw. is run on to the surface of a large quantity of boiling acid of 142° Tw., and the concentrated acid is run out continuously at the bottom by means of a siphon (a fixed tube from the bottom with an overflow at the top, is stopped up quickly by mud). He proposes to connect the bottom of the vessel with an acid egg, serving as a mud collector, and to pass the vapours escaping from the pan through a small tower like a Glover tower, fed with chamber-acid to such an extent that the gases issuing from it have a temperature of about 100° C.

The Galizische Karpathen Petroleum A. G. Vorm Bergheim, MacGarvey, and A. Gellen[3] (Ger. P. 271625 of 13th June 1912; Austr. P. 60565) concentrate sulphuric acid in a cast-iron apparatus, as shown in Fig. 69, consisting of a pan (*a*) provided with an outlet (*i*) for the concentrated acid, and heated by a direct fire, a lid (*b*), and a hood (*c*). The latter, as well as the lid (*b*), is heated from the outside by the fire-gases, in order to protect distilling vapours from condensation. Pipe (*d*) carries away the vapours; its lower part is surrounded also by fire-gases. Within the hood (*c*) there is a set of dishes (*f*), the lowest of which rests by means of the parts (*g*) on projections (*h*) attached to the sides of the pan (*a*). The cover (*b*) may also be shaped in such a way that it forms itself the lowest of the dishes (*f*). This dish is provided with a central opening, the margin of which is lower than the outer lip of the dish, so that the acid, after being previously concentrated on its way through the set of dishes, can run away in the centre of the last dish. A current of hot air may be aspirated through the apparatus, and several pans may be arranged alongside. The weak acid runs through *k* on to the top dish. All the acid vapours escape through *d*, either into a cooler or into a tower made of acid-proof material fed by cold acid, which is thereby heated and increased by the condensing distillate.

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[1] *J. Soc. Chem. Ind.*, 1907, **26**, 967.

[2] *Chem. Zeit.*, 1909, p. 478; *J. Soc. Chem. Ind.*, 1909, **28**, 653.

[3] *J. Soc. Chem. Ind.*, 1914, p. 463.

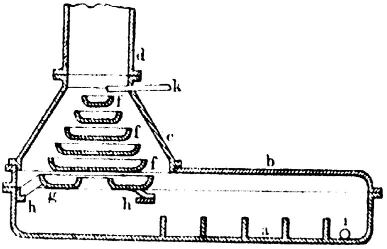

FIG. 69.

Morgan (B. P. 127652 of 14th May 1917, appl. 6831 of 1917) describes a small tower (4 ft. in diameter), having an acid-proof lining, in which is placed a series of shallow lipped basins (3 ft. in diameter), one above another, alternately on opposite sides of the tower on C.I. supports, so as to allow the acid to drop continuously into the basin below. Weak acid to be concentrated is fed into the top of the tower, and, in flowing downwards from basin to basin, is concentrated by the heat of the hot fire-gases passing up the tower. The basins act as baffles, causing the fire-gases to take a circuitous route. The upper basins are made preferably of ferrosilicon alloy, but near the bottom where the acid is stronger, they can be of cast iron. A slight draught is maintained on the tower, and the waste gases are exhausted at the top into scrubbers, and thence to the chimney. The concentrated acid passes away through a sump at the base of the tower. The sides of the tower are made in such a way that one or more can be removed for cleaning or repairs. (See Figs. 70 and 71.)

Dreyfus[1] (B. P. 101642 of 1916) concentrates sulphuric acid from 92 per cent. upwards in a cast-iron apparatus consisting of an outer cylindrical pan, fitted with a lid, and containing a series of concentric cylinders alternately supported by the pan and lid. The acid is fed into the centre, and travels alternately down and up to the outermost space, which it leaves by an overflow pipe. Advantage is taken of the fact that (*a*) 90 to 93 per cent. H_2SO_4 does not attack cast iron; (*b*) that in the concentration of H_2SO_4 the higher strengths are at the bottom; (*c*) that water is eliminated gradually by the extensive travel of the acid through a number of vessels.

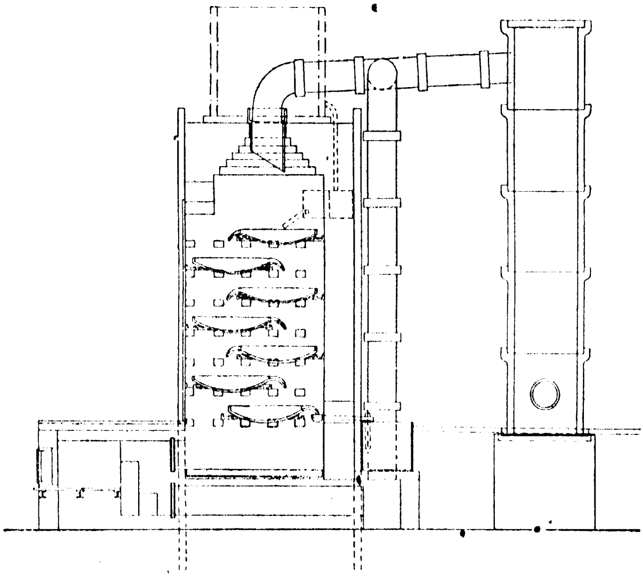

FIG. 70.

The Clayton Aniline Co.[2] (B. P. 11544 of 1898) employs ast-iron pans in such a manner that the acid of any desired trength is run on to the centre of the surface of heated acid ontaining not below 90 or 93 per cent. sulphuric acid, at the ame time withdrawing so much strong acid from the bottom of

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[1] *J. Soc. Chem. Ind.*, 1916, p. 1155.

[2] *J. Soc. Chem. Ind.* (*Abstr.*), 1899, 18, 494.

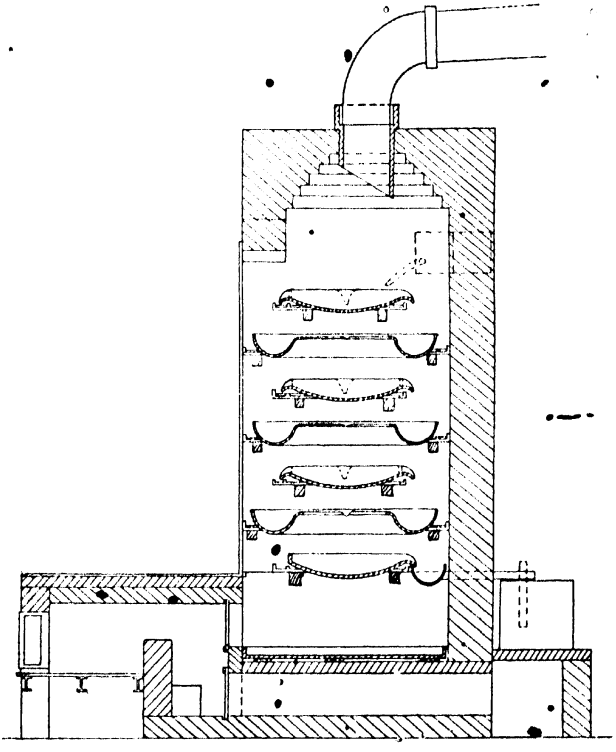

Fig. 71.

he vessel that the level remains constant. (A similar process s described in Gridley's U.S. P. 2[illegible]5495 of 1882.)

Dreyfus and the Clayton Aniline Co. (B. P. 788 of 1902) escribe a recuperator tower 4 to 8 ft. high, packed with acid-roof material, for use in conjunction with the above apparatus. The distilling vapours from the concentration pot enter at the bottom, and the weak acid to be concentrated is fed into the top of the tower.

The author is indebted to Mr P. Parrish of the South Metropolitan Gas Company, Phœnix Wharf, East Greenwich, S.E. 10, for particulars of an improved type of Dreyfus cast-iron concentrating pot. In the plant for the production of synthetic phenol, the capacity of the sulphonators is a function of the strength of sulphuric acid used in the sulphonation of the benzene. Pending the erection of an oleum plant, a cast-iron concentrating pot of the Dreyfus type was erected (1916) to increase the strength of the sulphuric acid from 93 per cent. to 96·5 per cent. H_2SO_4. A general arrangement of the plant, comprising four Dreyfus cast-iron pots, recuperator towers, fume collecting-box, graded coke scrubber, cast-iron coolers, etc., is indicated in Fig. 72.

The acid to be concentrated was discharged from railway tank wagons to wrought-iron storage boilers. In order to admit of feeding the acid to the recuperator of the Dreyfus pot by gravitation, an overhead lead storage tank was constructed, and this was filled by withdrawing the acid from the wrought-iron storage tanks to a cast-iron egg, and elevating by compressed air. To allow of a delicately-adjustable feed of acid to the recuperator towers, special feed-boxes were provided. The recuperator towers served a two-fold purpose. They preheated the cold feed acid prior to introduction to the pot; and, secondly, cooled partially the vapours and products of decomposition arising from the acid being concentrated in the pots.

In designing these towers regard was had to the probable temperature of the exit-gases. It was realised that if too much cooling was effected, dilution, rather than an accession of temperature of the feed acid, would occur. The importance of a special packing medium for the towers was recognised also. It was decided to line the recuperator towers with special acid and heat-resisting bricks (obsidianite), and to use Irish (Arklow) quartz as a "filling" medium.

Generally speaking, the Dreyfus pots used were of the standard design (3 ft. 4½ in. deep by about 3 ft. 6½ in. mean diameter), except that a special cast-iron shield was provided at the top of the pot to arrest the corrosion of the "acid level." The pots were seated on four curvilinear blocks, and the products of combustion from a coke fire passed through a pigeon-holed semicircular arch under the pot and around "wheel" flues, finally discharging into a chimney-stack, 32 ft. high by 2 ft. square, which chimney served for two pots. The hot acid was led into a cast-iron cooling-collecting pot, passing thence to a shute, the lead lining of which was protected by suitable trough tiles, bedded in a special cement constituted of silicate of soda and ground Volvic lava. The acid was discharged finally into a cast-iron egg, and blown to a wrought-iron storage boiler, arranged in such a way that the acid could be gravitated to acid tank barges, or to railway tank wagons, at will. The products of dissociation leaving the four recuperator

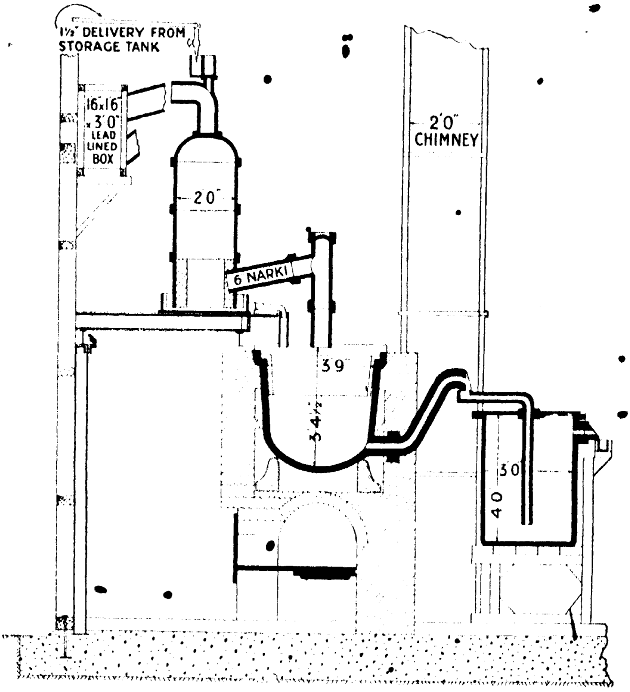

FIG. 72.

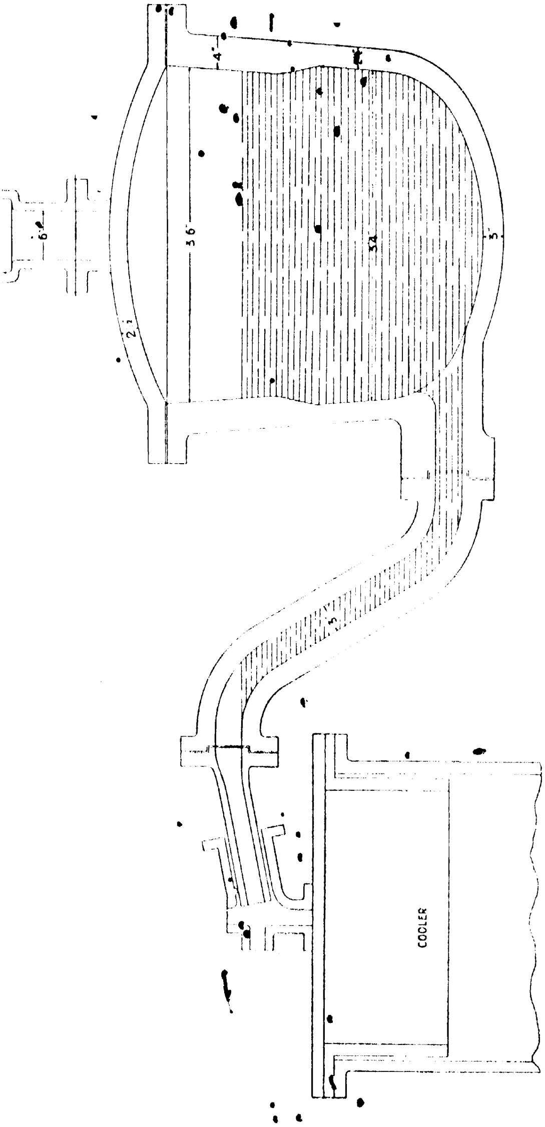

FIG. 73.

towers were collected in a lead box (24-lb. chemical sheet lead), water-sprayed, and a 12-in. diameter lead pipe conducted the gases to a coke scrubber, 12 ft. by 12 ft. by 6 ft. 6 in., arranged to afford downward flow or percolation of the condensed gases.

By the operation of a Kestner high-pressure regulus metal fan on the outlet of the condenser a suction of about 0·5-in. water-gauge was maintained on the Dreyfus cast-iron pots.

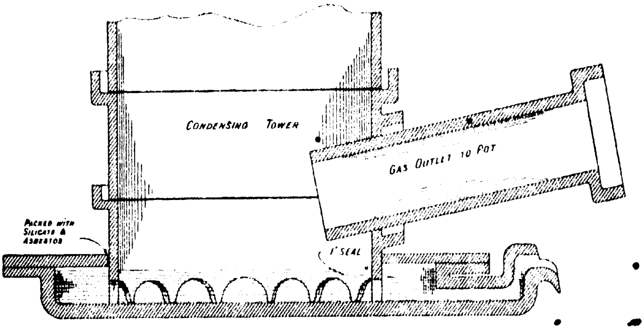

FIG. 74.

The plant, as described, worked continuously for about twelve months, and the weak points disclosed were:—

(1) Difficulty in maintaining the covers of the pots gas-tight.

(2) Heavy wear and tear on the lead collecting-box.

(3) Inadequate cooling facilities for the concentrated acid.

(4) Corrosion of the pots on the acid line behind the shield.

(5) Rapid "scoring" of the regulus metal valve affixed to the cast-iron acid eggs.

(6) Escape of acid fumes at the dish of the recuperator tower, and the point of discharge from the goose-neck to the cooling-collecting cast-iron pots.

The difficulties enumerated under 1, 4, and 6 were overcome effectually by modifying the design of the Dreyfus pot and accessories, as indicated in Fig. 73, and by arranging a gas-tight cast-iron cover to the dish of the recuperator towers, as shown in Fig. 74.

Profuse water-cooling of the lead collecting-box reduced the wear and tear at this point (No. 2). The adoption of a special

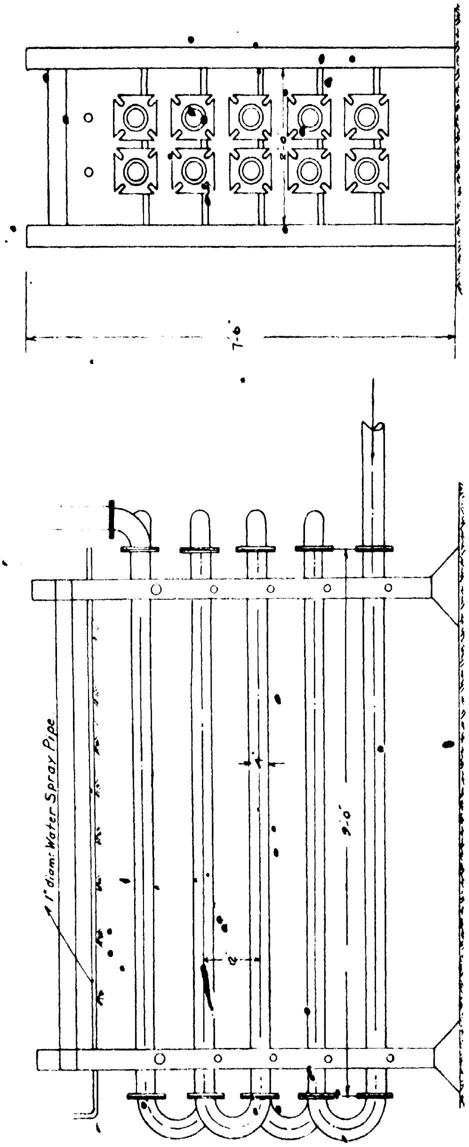

FIG. 75.

serpentine water-sprayed cast-iron cooler afforded adequate cooling capacity for the concentrated acid, and thus enabled No. 3 difficulty to be overcome. Details of this cooler are shown in Fig. 75. The square flanges have a raised circular machined flange, and all joints are made with ⅛-in. asbestos sheet, thoroughly immersed in silicate of soda. With the reduction of temperature of the final acid accompanying the installation of the above cooler, and by using a King's cast-iron wedge-shaped faced disc valve, the "scoring" trouble indicated under No. 5 heading was surmounted satisfactorily.

With the incorporation of the above modifications, the plant was converted eventually into a fool-proof one, which was capable of concentrating 18 tons of sulphuric acid from 93 per cent. H_2SO_4 to 96·5 per cent. H_2SO_4 per day. The control of the plant was effected by maintaining the temperature of the acid at a point approximately 6 in. from the bottom of the pot at 315° C., and by determining carefully the specific gravity of the condensed acid leaving the coke scrubber. Immediately the specific gravity of the condensed acid exceeded 148° Tw., it was known that dissociation, as distinct from concentration, was occurring, and constant attention was directed to this point. Samples of the final acid were collected each shift, and the tests recorded prominently in the Dreyfus plant, for the guidance of the process-men and foremen.

It should be noted that the capacity of the pots allowed of about twelve hours' contact of the acid in the pot. The cast-iron pots were cleaned about every two months, and the coolers every three months.

It was found that a 1-in. cast-iron overset siphon answered admirably for withdrawing the supernatant acid from the pots and coolers. Invariably the acid so removed was cooled by passage through a portable cast-iron serpentine cooler. The cast-iron pots had to be entered in order to remove the sludge, but in the case of coolers, provision was made for "sludging off" the sediment by flushing. Altogether 8000 tons of concentrated sulphuric acid was produced, and twelve pots were used in all—four of which were intact when the plant ceased finally to operate. The average coke consumption was 2·4 cwt. per ton of final concentrated acid, and the respective proportions of final concentrated acid (96·3 per cent. H_2SO_4) to condensed acid (80 per cent. H_2SO_4) were as 81·37 is to 14·3. The loss in concentration was 4·3 per cent.

Cast-Iron Pans Protected by Enamel or Otherwise.

It might be thought that *enamelled* cast-iron might be more suitable for the concentration of sulphuric acid than ordinary cast iron. In fact, Roder[1] proposed enamelled cast-iron boilers, and indicated a special kind of enamel for them: 1 part of powdered burnt alum, 4 parts of red-lead, and 2 parts of pure silica, are to be melted together; the fluxed mass is to be cooled with water, dried, powdered, and 15 parts of it intimately mixed with 20 parts of pure silica and 3 parts of tin oxide. The whole is ground up with spirit of turpentine laid with a soft hair-brush on the smoothly turned inner surface of the boiler; and this is repeated three or four times, each coat being allowed to dry first. The enamel is then fixed by fusing on as usual. But even the best enamel will resist only a very short time the boiling sulphuric acid and the uneven expansion and contraction of metal and enamel at the very greatly differing temperatures which occur in that process, and his proposal has had no practical success.

Wolters (Ger. P. 15639) states that by heating a mixture of alkaline pyrosulphate with concentrated sulphuric acid in iron vessels, a crust of iron sulphide is formed which protects the iron during distillation, so long as the pyrosulphate is left in the vessel.

Tate[2] mentions an apparatus constructed by West in 1883 on the continuous system, with an enamel or porcelain lining; nothing is known as to its success.

Dyson[3] (B. Ps. 17699 of 1893 and 27769 of 1896) has made a cascade-apparatus, consisting of iron pans lined with a special enamel, connected by U-shaped siphons, which carry the acid from the bottom of each vessel into the upper part of the next. A set of eighteen pans produces 21 tons of strong acid per week. This apparatus is stated to require 6 cwt. of coke per ton of acid. Some more details are given in *Chem. Trade J.*,

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[1] *Dingl. polyt. J.*, **111**, 397.

[2] *J. Soc. Chem. Ind.*, 1894, p. 208.

[3] *J. Soc. Chem. Ind.*, 1894, **18**, 1059; 1897, **16**, 913.

92, 339. Chamber-acid of 100° Tw. is employed, and 100 tons acid of 168° Tw. is produced in one apparatus in forty-three days, with a consumption of 23¼ tons of gas-coke. In 1902 several plants on this system were in operation in England.

Seckendorff[1] proposed to concentrate the acid in flat-bottomed iron retorts completely surrounded by fire. The retorts are to be filled with lead sulphate, sand, or gypsum; chamber-acid is to be run in till a paste is formed, and the retorts are then to be heated. The watery vapour first appearing is conducted into the chambers; the concentrated acid coming after this is to be collected in glass or stoneware vessels, and is said to be very pure, free from iron, and as concentrated as that from platinum; nor is the iron retort said to be acted upon very strongly. Probably this plan has never been actually tried at all.

J. Gridley (U.S. P. 265495) recommends cast-iron pans, protected at the top by an asbestos cement against the action of the acid. The pan is filled up to the proper level with acid of 167° Tw., and is fed in such a manner that the concentration never sinks below 163° Tw., in which case the pan is not acted upon. (This strength, equal to less than 90 per cent. H_2SO_4, is much too low to prevent action on the iron.) The corresponding British patent, No. 4709 of 1882, has not been proceeded with.

Flanagan[2] (B. P. 3530 of 1901) employs enamelled cast-iron pans, with water-cooled leaden hoods, placed at different elevations. There seems to be no new principle whatever in this invention.

The Chemische Fabrik List, E. de Haen (Ger. P. 197074), produces acid-proof vessels, apparatus, and electrodes by pressing *tantalum* hydride into moulds, and converting the moulded pieces into tantalum metal by heating them gradually, ultimately for two hours to a white heat, and slowly cooling. The hydrogen given off is first removed by a water air-pump, and later on by a mercurial air-pump, and with as good a vacuum as possible.

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[1] *Wagner's Jahresber.*, 1855, p. 56.

[2] *J. Soc. Chem. Ind.*, 1901, **20**, 1112.

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CHAPTER IV

CONCENTRATION OF SULPHURIC ACID IN A CURRENT OF HOT GASES

STODDARD[1] and Galletly[2] proposed to force a current of cold air into sulphuric acid heated in lead pans. If the temperature be 150° C., acid of 140° Tw. is stated to be obtainable in this way. The method was unsuccessful on a practical scale, as only cold air was employed; and the first use of hot air seems to have been made by Gossage in 1850. Gossage's apparatus is fully described and illustrated in our 2nd edition, pp. 735 *et seq.* It consists of a double-shelled lead tower, with an air space between the two shells; the tower is packed with pebbles, over which the dilute acid trickles down, and this acid is concentrated by a current of air, heated up in a parallel series of perpendicular iron pipes, and passing through the tower in a downward direction. This apparatus has never come into use; its faults are the following:—

The air must be made nearly red-hot, and thereby the upper lead pipe always melts; the air, charged with vapour, travels in the same direction as the acid, and therefore again gives up its water to the latter as it becomes more highly concentrated; all acid escaping along with the hot air is lost in the chimney. Although some of these faults might be avoided by changing the details of construction, the apparatus seems hardly ever to have been employed in practical work. According to the 41*st Alkali Inspector's Report* (p. 83), a brick tower for the concentration of sulphuric acid, which had been stopped for alterations, had not been started again.

Gossage's plan has been re-invented by Costelle, without any additions.[3]

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[1] *Chem. News*, 28, 167.

[2] *Chem. News*, 24, 106.

[3] *Chem. News*, 20, 10[illegible].

S. T. M'Dougall (U.S. P. 289292) employs a tower, heated from without, filled with dishes, over which the acid flows down, whilst heated air ascends in the tower (*cf.* Nobel's patent, p. 107).

Similar in principle, although very different in detail, is the hot-air concentrator patented by the International Vacuum-Eismaschinen-Verein (Ger. P. 33172). It does not seem to have answered, as the same firm a year later took out a patent (No. 38015) for a totally different apparatus, working with steam, as already mentioned on p. 69.

Finch[1] (B. P. 2207 of 1886) combines an evaporating furnace with two towers filled with refractory material. The furnace-bed is formed by a lead tank, lined with sheet asbestos, and upon this with silica bricks. The roof of the furnace is formed of silica bricks and covered outside with lead. The weak acid first passes through the towers and then into the furnace; the fire-gases make the opposite way. (It is very unlikely that an apparatus such as described will be able to stand the wear and tear of the process for any length of time.)

Fontenille (Ger. P. 37713) causes hot air to issue by means of many holes from a pipe at the bottom of a vessel filled with sulphuric acid; the vapours pass in a zigzag manner over several plates, over which fresh acid is running down. (It is not stated what material the vessel is to consist of.)

Gridley (U.S. P. 240248) applies strong heat to the under-surface of a thin body of dilute acid, and at the same time a blast of superheated steam or hot air to the upper surface, removing the vapours as they rise.

Norsk Hydro Elektrisk Kvaelstofaktieselstab, Christiania[2] (B. P. 132704 of 22nd January 1919, appl. 1637 of 1919; U.S. P. 1353448, 21st September 1920). Nitrous gases at a temperature of 1000° C. may be employed for the concentration of sulphuric acid if they are first mixed with a proper proportion of exhaust gases from the concentration chamber, by which means they are reduced to 500° to 600° C., and decomposition of sulphuric acid avoided. The remaining exhaust gases are saturated with moisture, which is readily removed by condensation.

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[1] *J. Soc. Chem. Ind.*, 1887, p. 216.

[2] *J. Soc. Chem. Ind.* (*Abstr.*), 1919, p. 817.

The Soc. an. la Fabrique de Soie Artificielle de Tubize[1] (B. P. 10386 of 1915; Fr. P. 479320) concentrates sulphuric acid by means of elements heated from the outside, arranged in steps, and communicating in such a manner that the acid flows downwards; whilst the vapours produced pass from the lower to the upper elements. The elements may consist of glass or platinum for strong acids, and of ordinary or hard lead for weak acid.

Pfannenschmidt and Moss[2] (Fr. P. 474995 of 1914) employ a cascade of shallow square trays, heated by waste heat. The hot acid falls then through a column of hot gases, followed by a cold air for cooling in a second chamber. The chambers are provided with perforated plates to convert the acid into a fine spray.

Vetterlein and Chem. Fab. Zu Schoningen[3] (Ger. P. 307564 of 27th August 1916) concentrate acids by passing the liquid to be evaporated and the heating gases in contact in opposite directions, and in a horizontal zigzag path through the evaporator, consisting of a metal pan built in a masonry setting, and through a preliminary tower built above one end of the metal pan. The liquid is sprayed into the top of the tower, which may be filled with packing, and meets the ascending exhaust gases from the main evaporator; it is collected in the pan beneath and flows in contact with the furnace gases through the pan, which is divided by partitions into zigzag channels, to the outlet near the furnace. The pan may be constructed of wrought iron and supported on pillars in the masonry setting. In the evaporating space, all baffling obstructions are avoided, and doors are fitted in the walls at the ends of the channels, to facilitate cleaning of the trough.

Lennox[4] (B. P. 23919 of 1914) employs a rotating corrugated drum, dipping into a trough mounted on sliding rods, which is divided into compartments for every corrugation; the whole is enclosed in a casing. The compartments communicate with one another at alternate ends of the partitions. Hot air or the like is passed through the drum, and the acid drops on to the drum at the end remote from the hot air inlet, and at a point in advance of the axial plane; the concentrated acid is withdrawn from the last compartment of the trough at the hot air inlet end.

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[1] *J. Soc. Chem. Ind.*, 1916, p. 537.

[2] *J. Soc. Chem. Ind.*, 1915, p. 1142.

[3] *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 767.

[4] *J. Soc. Chem. Ind.*, 1915, p. 1054.

H. W. Jones and the Armour Fertiliser Works[1] (U.S. P. 1183207 of 1916) concentrates acids by allowing them to trickle down in the form of alternate pools, and films over an irregular inclined surface in an enclosed chamber, while a current of hot gases passes over it. The gases are introduced at the lower part of the chamber, and directed by means of a baffle, on to the surface of the acid. The concentrated acid collects at the bottom of the chamber, and the moisture-laden gases leave at the top.

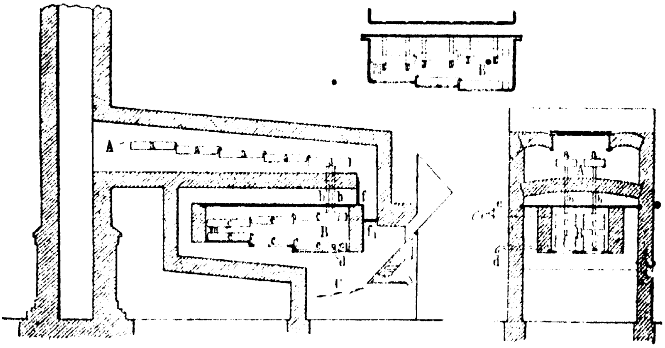

FIG. 76. FIG. 77.

A new patent of Zanner's (B. P. 19841 of 1914; Fr. P. 462016; Ger. P. 260555) describes an arrangement illustrated in Figs. 76 and 77. The first concentration takes place in two rows of quartz boxes (*a a*) placed in the upper space, A, and connected with one another by overflows. Where the acid need not be specially pure, these boxes may be left open, so that the acid is heated also on the top. The aqueous vapours formed are carried along by the fire-gases into the chimney. If the acid is to be pure, the boxes are provided with thin covers, with holes protected by caps for the escape of the aqueous vapour. The first concentration may, of course, be effected also by lead pans, in a spray tower, etc. The main concentration takes place in the muffle, B, built of material proof against acid at high temperatures: such as fire-bricks, quartz, cast iron, etc. It is entirely closed, and heated outside by fire-gases. Within the muffle there are open boxes, *c c*, made of quartz, which receive the previously concentrated acid by the pipes *b*, and after concentration allow it to run out by the pipes *d*. The acid vapours formed here are conducted by pipe *e* to the cooling worm or box.

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[1] *J. Soc. Chem. Ind.*, 1916, p. 736.

The number of quartz boxes in the muffle (B) corresponds to the demands made upon the performance of the apparatus. These boxes may be suspended or placed on the bottom of the muffle, or both. In some cases (*i.e.* when concentrating to 97 to 98 per cent. H_2SO_4) the last boxes (which are in this case preferably made of cast iron) are fixed in the bottom of the muffle (B) in such a way that their lower surfaces are touched by the fire-gases as directly as possible, without admitting them into the interior of the muffle. This last case is the one shown in the diagrams. For intensive work the muffle may be worked with a vacuum. Instead of a fireplace, as shown at C, the heating may be effected by a gas-producer. The draught is regulated by slides at f and f_1.

Davis[1] (B. P. 128396 of 19th June 1918, appl. 10127 of 1918) describes a "Trepex" concentrator, which works on the principle of passing the hot gases of combustion from a furnace through a spray of the acid which is to be concentrated. The apparatus is shown in Fig. 78.

It consists of a furnace fired with coke, or other smokeless fuel, and an evaporating chamber, into which the gases of combustion are passed. The chamber is proportionate to the amount of work required to be done; but for concentrating, for example, dearsenicated acid of 105° Tw. to 145° Tw. at the rate of 20 tons of strong acid per twenty-four hours, only about 150 cub. ft. of space is required in the evaporating chamber. The acid to be concentrated lies on the bottom of the chamber to a depth of a few inches, being fed in continuously at the end remote from the furnace, and travelling forward gradually to the exit at the end near the furnace. The device for spraying up the acid into the chamber consists of a shaft carrying fanners made of a suitable material, fixed

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1919, p. 628.

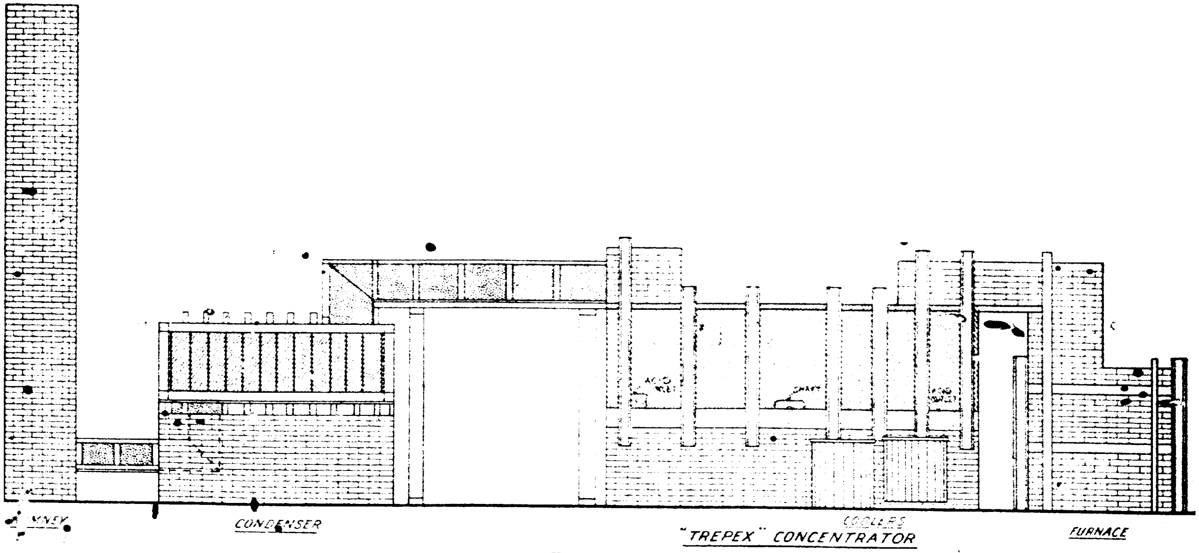
MNEY
CONDENSER
ACID WELL
SHAFT
COOLERS
"TREPEX" CONCENTRATOR
FURNACE

Fig. -8

across the evaporating chamber at right angles to the flow of the gas. The position of this shaft is shown in Fig. 78. The rotation of this shaft at the correct speed fills the chamber from end to end with a fine spray of the acid to be concentrated; in this manner, owing to the very excellent contact between the hot gases and the acid, a high efficiency is secured, and an evaporation of 5 lb. of water per pound of coke consumed in the furnace is obtained. When concentrating up to 145° Tw. there is very little fume produced, and the condenser shown in Fig. 78 is not absolutely necessary, although it is preferable to have it installed.

As there is no back pressure produced in any part of the plant, ordinary chimney draught is sufficient to work it. The power absorbed by the rotating shaft does not exceed one-half h.p., and is supplied by a small electric motor. The evaporating chamber may be constructed of special acid-resisting blocks, with a lead dish to prevent any escape of acid. The acid is not in contact with any lead-work at any time during the concentration. The acid inlet and outlet are only about 12 in. difference in level, so that pumping of acid is reduced to a minimum. The cost of a complete installation, including furnace, "Trepex" evaporating chamber, condenser and coolers, for an output of 20 to 24 tons per twenty-four hours of 145° Tw. acid is approximately £1200 to £1500 (June 1921). Up to the present the plant has not been installed for producing rectified acid (93 to 94 per cent. H_2SO_4).

The 53*rd Alkali Inspector's Report for* 1916 refers to the Davis concentrator, as follows:—

"This consists of a leaden chamber, 15 feet long by 5 ft. high by 2 ft. wide; the flow of acid is 3 in. deep, and is thrown up by paddles on the Porion System; hot gases from a large coke fire meet the flow of acid on the counter-current principle. With a temperature of 310° C. to 320° C., acid is concentrated from 110° Tw. to 144° Tw., and the exit-gases pass through a condenser to a leaden chimney. Initial difficulties are being overcome, and a steady flow of acid at 144° Tw. is produced. This seems a hopeful type of plant, capable of much work in a small space, if of proper construction and design."

According to the 54*th Alkali Inspector's Report for* 1917, the Davis concentrator continued in operation with improved efficiency. The initial difficulties encountered in the first works where it was installed were overcome largely, and latterly much more regular and satisfactory work was effected. Additional units are now in operation or in course of erection at different works, so that wider and more varied experience will be acquired.

According to the 55*th Alkali Inspector's Report for* 1918, the Davis concentrator was used for bringing chamber-acid up to about Glover acid strength, and gave satisfaction.

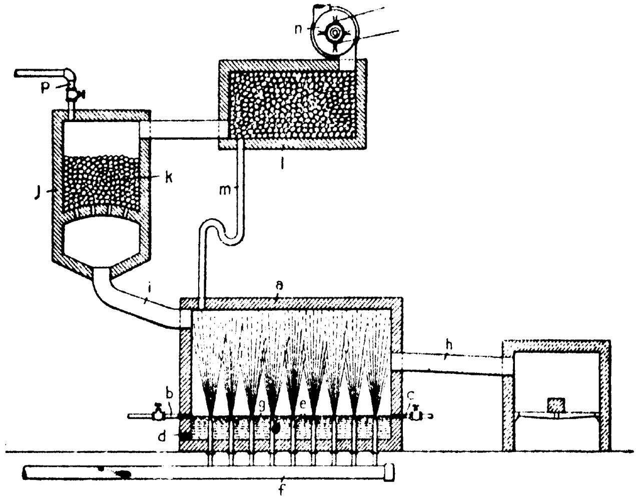

FIG. 79.

Skoglund[1] (U.S. P. 12[illegible]109 of 3rd July 1917, appl. 4th May 1916; B. P. 113551 of 14th May 1917, appl. No. 6841 of 1917) concentrates sulphuric acid by passing hot gases through a spray of acid. A current of compressed air is injected beneath the surface of a shallow body of acid, to create circulation therein, and to blow a portion of it into a vertically-directed spray, so that the spray, after coming into contact with the hot fire-gases, falls back again into the body of the acid under treatment. As shown in Fig. 79, the apparatus consists of a closed box (*a*) made of lead and lined with an acid-resisting material. The box is provided with an acid-inlet (*b*), and at the opposite end an acid outlet (*c*), and one or more plugs (*d*) for the removal of impurities from the bottom of the vessel. In the bottom of the vessel (*a*) a series of nozzles (*e*) is placed centrally, and in alignment with one another, so that their openings lie a short distance below the surface of the acid. These nozzles are connected with a source of compressed air (*f*), by means of which the acid is blown into a series of sprays, as indicated in the drawing (*g*). The fire-gases are admitted at *h*, and at the opposite end of the vessel the pipe (*i*) connects with a tower (*j*) packed with acid-proof material (*k*). This, in turn, is connected with a suitable condenser (*l*), from which any condensed liquor runs back to the vessel (*a*) by means of the pipe (*m*). The gases are drawn through the plant by means of a suitable fan or blower (*n*). The weak acid to be concentrated (*p*) is fed into the tower (*j*), which serves not only to preheat the acid, but also to condense acid vapours carried forward by the hot gases, from concentration vessel (*a*). This plant is built by the Pratt Engineering Co. of New York, and, according to *Bulletin* 184 *of the Bureau of Mines* (p. 140), the fuel consumption averages around 12 gall. of oil per ton 167° Tw. acid concentrated from 105° Tw. acid.

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[1] *J. Soc. Chem. Ind.*, 1917, p. 925; *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 182.

THE KESSLER CONCENTRATION PLANT.

The most successful apparatus for the concentration of sulphuric acid in a current of hot air is that of J. Kessler[1] (B. Ps. 19215 of 1891; 26169 of 1898).

The conditions to be fulfilled in an apparatus of this type are as follows. The current of hot air must be brought into contact with such a large surface of liquid that its temperature is immediately reduced to a great extent. The air must thus become saturated completely with steam and acid vapour. The apparatus must resist, not merely the action of the hot air and hot acid, but it must be constructed in such a manner that the deposits and crusts inevitably formed in the process of concentration do not give any trouble. Under these conditions, the acid can be concentrated far below its boiling-point. For good evaporation, large volumes of moderately hot gas rather than a high temperature are required. The lower part of the apparatus is called by Kessler, the "Saturex," because it saturates the fire-gases with acid vapours, and it quenches the greater part of their heat. The acid vapours contained in the hot gases are retained in the upper part of the plant, called the "recuperator," mounted above the saturex. This part of the apparatus acts as a reflux condenser, and resembles the dephlegmating column employed in the rectification of alcohol. It is fed with chamber acid, which traverses each plateau of the recuperator in turn, and, in doing so, it meets the hot air and vapours issuing from the saturex and drawn through the liquid acid by applying suction at the end. In the recuperator the temperature sinks to between 85° and 100°: this causes nearly the whole of the acid vapours to condense, while the steam is not condensed, nor is there much fresh steam formed here. This is important, since any concentration of the acid in this place would cause deposits which would soon obstruct the holes in the trays. The saturex is built in the form of a shallow trough of volvic lava or other acid-resisting material, surrounded by a thick lead jacket, upon an open foundation. Between the bottom and the cover of the saturex there are several baffles, which force the fire-gases entering at 300 or 450° to impinge on the surface of the acid exposed in the bottom of the saturex, and, when passing from one of these baffles to another, through the acid itself. The temperature of the gases drops quickly to 150°, and at the same time the acid rapidly loses water and some acid vapour, and runs out of the apparatus in a concentrated state to the cooler.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1892, p. 414; 1900, p. 246.

The early form of apparatus is described very fully, with detailed drawings, in our fourth edition (pp. 1190 to 1200), but is omitted here, as it is now out of date. Similarly, the description of the "Radiateur" (B. P. 21376 of 1900) is omitted also, as it did not prove as practicable and as robust a form of apparatus as the saturex type, and therefore was never developed.

The latest modification of the Kessler apparatus is that of Teisset and Prat[1] (Fr. P. 398212 of 1908; B. P. 14300 of 1909; Ger. P. 229676; U.S. P. 993125).

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1909, **28**, 937; 1910, **29**, 950; *Z. angew. Chem.*, 1911, **24**, 184; *J. Soc. Chem. Ind.* (*Abstr.*), 1911, **30**, 748.

The author is indebted to M. J. Teisset-Kessler of Clermont Ferrand for the following particulars, as well as the drawings. Figs. 80 to 89 (June 1921).

The alterations on the old form of apparatus which possessed three longitudinal baffles in pumice stone in the saturex, had an intermittent gas producer, and was worked by means of a blower, are as follows:—

(1) The longitudinal baffles in pumice stone have been suppressed, and their place taken by transverse baffles in volvic stone.

(2) The intermittent gas producer has been replaced by a simple continuous producer.

(3) Instead of the steam jet, a high-pressure fan has been substituted, of a simple and robust type.

The main improvements derived from these alterations are as follows:—

The longitudinal baffles in pumice stone in the old saturex, which were slight and fragile, broke away easily, especially during the cleaning of the saturex. It followed, therefore, that the hot gases, which should have forced their way through the acid in passing under these baffles, escaped instead by the gaps in the stones. Through the diminution of the travel of the gases in the saturex, they arrived in the recuperator at too high a temperature, which led to the breakage of the porcelain calottes.

With the system of strong transverse baffles in volvic stone, the gases, when passing between them, lick the surface of the acid. Under the action of the suction from the fan, the acid tends to bank itself up towards the end of the saturex nearest the recuperator, where the hot gases should escape, so that they find the space more and more reduced, which forces them into still more intimate contact with the surface of the acid. Numerous experiments made with this new construction of the interior of the saturex have shown that the work done in the saturex is exactly the same as that obtained in the old process with longitudinal baffles. The baffles in the new method of construction of the saturex are stronger, less expensive to erect, and much easier to replace.

By the adoption of the new type of simple gas producer, it is possible to work the plant continuously without any stoppage. Previously, with the old intermittent gas producer, it was necessary to stop the plant for a period of one and a half to two hours, in order to clean and recharge the fire. In the new type, these two operations can be carried out during the working of the plant, with the result that there is an increase in production of concentrated acid per twenty-four hours in excess of the guaranteed quantity for the same time.

The third modification, *i.e.*, the substitution of the steam jet by a high-pressure fan, has effected a notable economy in the consumption of fuel required for draughting the plant, as the power required to drive the fan (3 to 4 H.P.) represents a consumption of steam one-seventh or one-eighth that formerly taken by the blower. In addition the working of the plant is rendered much more regular, since the pressure of steam varied with that of the boiler, and hence the blower gave a varying speed to the gases passing through the apparatus, so that the degree of concentration of the acid was not constant.

With the new apparatus the gases maintain always a constant speed; hence there is a greater regularity in the degree of concentration of the acid and a smaller consumption of coke in the gas producer.

The latest modification is shown in Figs. 80 to 89.

The installation consists essentially of (1) a gas producer; (2) the apparatus itself composed of the "Saturex" and of the recuperator, made of five trays or plateaux; (3) a condenser packed with coke; (4) a cooler for the concentrated acid; (5) a fan for drawing the hot furnace gases through the plant.

Gas Producer.—The furnace for producing the hot gases which are drawn through the plant is shown in Fig. 84.

The shell is built of ordinary brick, 220 mm. thick, on a concrete foundation, and braced with iron buckstaves, and occupies a space of 3 metres by 3 metres. It is lined 480 mm. thick with a suitable firebrick, and is divided into two similar compartments by a midfeather wall, 330 mm. thick. In this way two combustion chambers are formed, each 1·600 metres wide by 0·740 metres deep by 1·840 metres high above the fire bars. Each grate is formed of C.I. grate bars of the ordinary type, placed 800 mm. above an ashpit, which is closed in front by a sliding door. Above this is fixed a cast-iron plate having a door opening 500 mm. wide by 350 mm. high, at such a height that the bottom of it is on a level with the grate bars. Each furnace is charged from the top through an opening 400 mm. by 350 mm., communicating with the producer chamber, and is sealed by means of a heavy firebrick slab. The producer gas leaves each furnace through an aperture, approximately 480 mm. by 500 mm., into a mixing chamber, where the gases from each producer meet and mix together with secondary air.

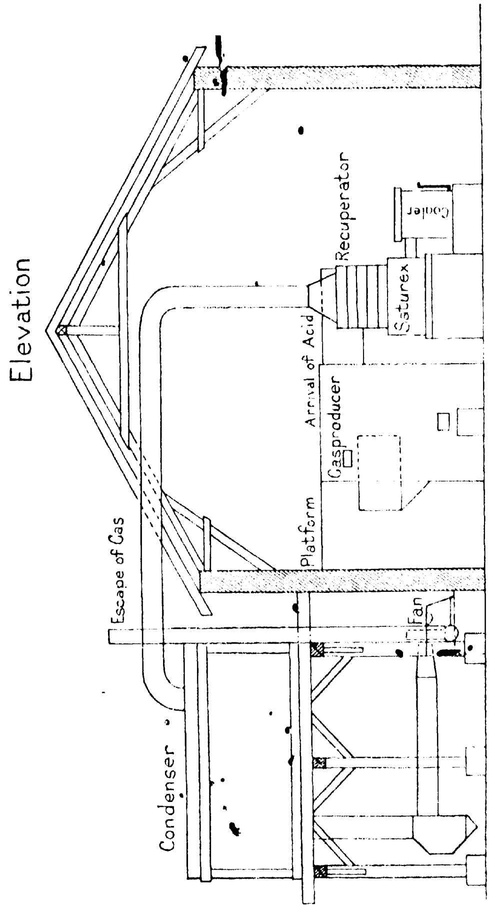


FIG. 80.

The shell of the furnace is pierced at one side by a flue (520 mm. by 200 mm.) leading from below the fire grate and rising vertically until it meets with another flue at the top of the furnace and enters the mixing chamber at a point adjoining the gas outlets from the furnaces. A sliding damper is fitted in the vertical flue to regulate the volume of secondary air admitted to the mixing chamber. From the mixing chamber the hot gases pass through a flue to the saturex. Port-holes

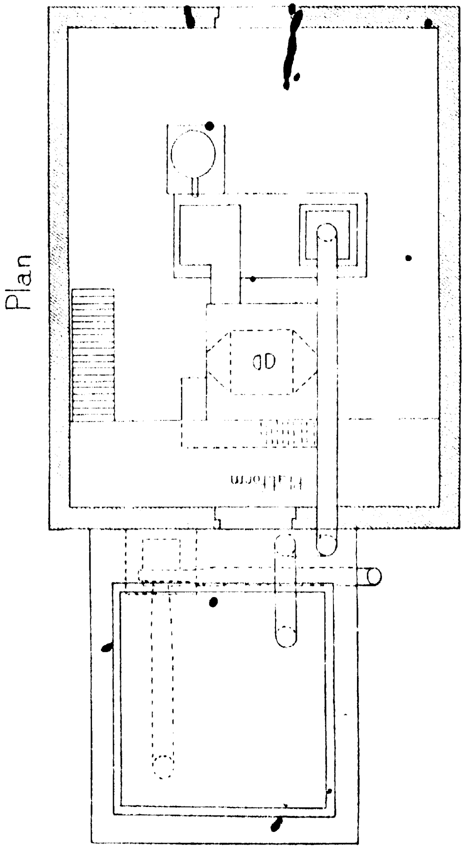


Fig. 81.

are fitted at various points in the flues, to allow for inspection and cleaning.

The two furnaces are worked alternately. Assuming No. 1 compartment is charged with coke and furnishing gas to the producer, then No. 2 compartment is charged as follows: First the firebrick slab covering the charging hole is removed; then the opening of the gas flue from the furnace into the mixing chamber is closed by means of a special brick, in order to prevent the passage of dust from the fire grate into the main gas flue. The fire grate is then cleaned thoroughly, and a fresh charge of coke added. As soon as the coke is ignited satisfactorily, the firebrick slab is replaced on the charging hole, and the gas admitted again to the mixing flue. No. 1 compartment is charged in a similar manner when its coke is exhausted, while No. 2 compartment furnishes the apparatus with gas.

Saturex.—Figs. 85 and 86 show the latest design of apparatus No. III. (*bis*).

Fig. 85 is a longitudinal section through the line CD. Fig. 86 is a plan through the line AB. Fig. 88 is a cross section. Fig. 87 is an elevation of the plant.

The saturex consists essentially of a shallow volvic trough, 2·72 metres long by 1·10 metres wide (internal dimensions); 3·32 metres long by 1·70 metres wide (external dimensions), built up in sections, and enclosed in a jacket of 10 mm. lead, a little sand being put between the stone and lead. The hot fire-gases enter from a firebrick flue at M, and, passing under a series of seven transverse baffles built of volvic lava, 25 cm. wide, are forced to impinge on the surface of the acid contained in the bottom of the saturex. The heat of the gases is reduced quickly by the contact with the acid liquid, which runs in the opposite direction to the travel of the gases. At the same time the acid loses its water, and also some acid vapour, and passes out of the exit pipe in a highly concentrated condition. Cleaning holes are provided in the saturex, between each barrier, and also at each end, so that the deposits and incrustations can be removed readily.

The gases leave the saturex saturated with aqueous vapour, and, passing over the shallow dish (D), enter the recuperator, which consists of five superimposed trays or plateaux, also in volvic lava (1·10 metres long by 1·10 metres wide, internal

THE KESSLER CONCENTRATOR

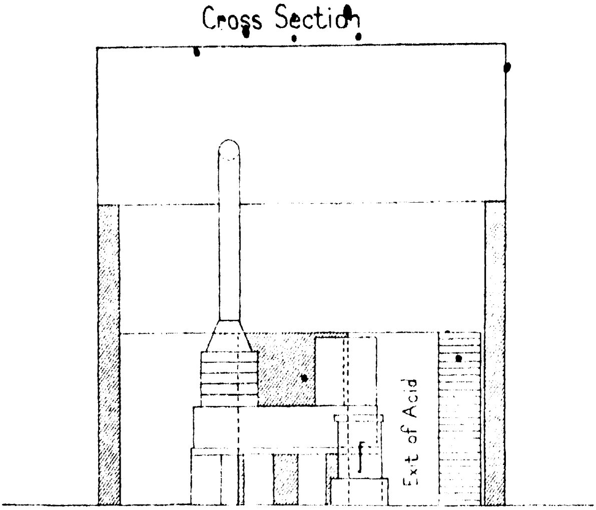


FIG. 82.

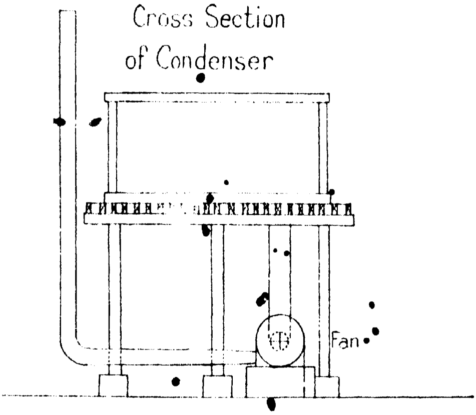


FIG. 83.

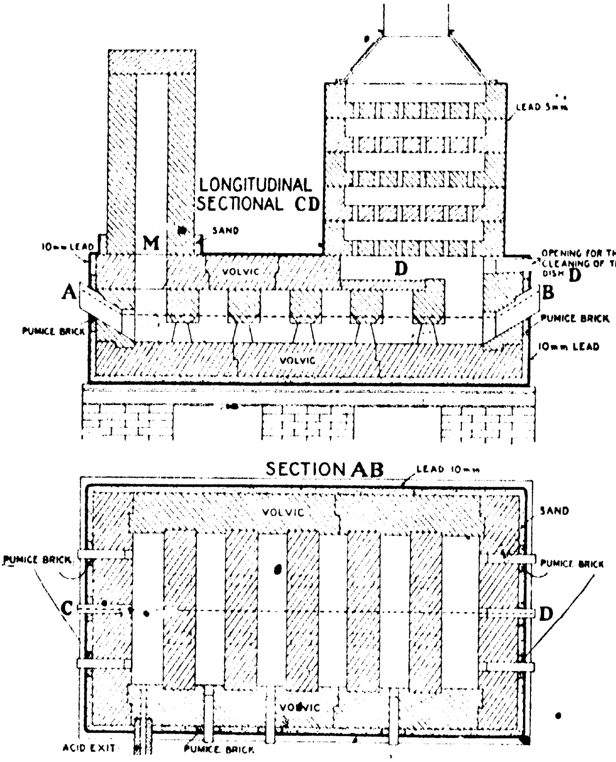
dimensions). Each tray is provided with twenty-four holes, covered by a luted bell or "calotte," as shown in Fig. 88. The acid to be concentrated is fed into the top of the recuperator, and lutes are placed right and left in each succeeding plateau, so that the acid flows across each plateau, while the hot gases bubble through it No acid finds its way through the passages in the calottes and over the edge of the calotte supports. The gases, bubbling up through the luted holes, are brought into such intimate contact with the acid that the temperature comes down to 90° to 100° C. at the top. At this temperature only aqueous vapour can exist, so that all the acid vapour is condensed before the gases get out; a small quantity of acid mist carried away by the exit gases is retained by the coke scrubber. The colourless concentrated acid is run out of the saturex at E, through a volvic pipe into a lead cooler, and flows away to storage tanks. The consumption of coke varies from 18 to 20 per cent. of the weight of finished acid for acid of 96 per cent. H_2SO_4. The calottes are made in porcelain or in fused silica ware; and the draught on each tray is recorded by means of a series of manometers. The breakages of these calottes cause a short circuiting of the gases; and this is detected by noting any variation from the normal in the suction of the manometer tube on each tray.

As a further guide to the working of the plant, the temperatures of the acid and gas are recorded by means of thermometers in various parts of the apparatus. The following figures show the average results obtained when the plant is working normally:—

Temperature of acid in top plateau	90·100°
„ „ „ bottom plateau . . .	190-200°
„ „ „ entering cooler . . .	210-230°
„ „ gases leaving Kessler . . .	125-145°
„ „ „ entering scrubber . . .	105-120°

Cooler.—The design of cooler varies, but consists essentially of a leaden vessel fitted with coils through which cold water is circulated. The hot acid runs into the centre, and passes down a stand pipe to the bottom of the vessel. (Vitreosil pipes give excellent results for this work.) The cool acid flows away from the top of the cooler to storage tanks.

Condenser.—From the top of the recuperator the gas passes through a lead-covered stoneware pipe to the top of the condenser (Fig. 85). This consists of a lead-lined box (5 metres by 7 metres by 2·5 metres, internal dimensions), built



Figs. 85 and 86.

up of a wooden framework on a timber platform carried at a suitable height above the floor level. The box is sheeted with thin wooden planks, and strengthened with round iron tie-rods at intervals. It is lined with 4 mm. lead on the bottom and sides, and covered with 3 mm. lead supported by lead straps

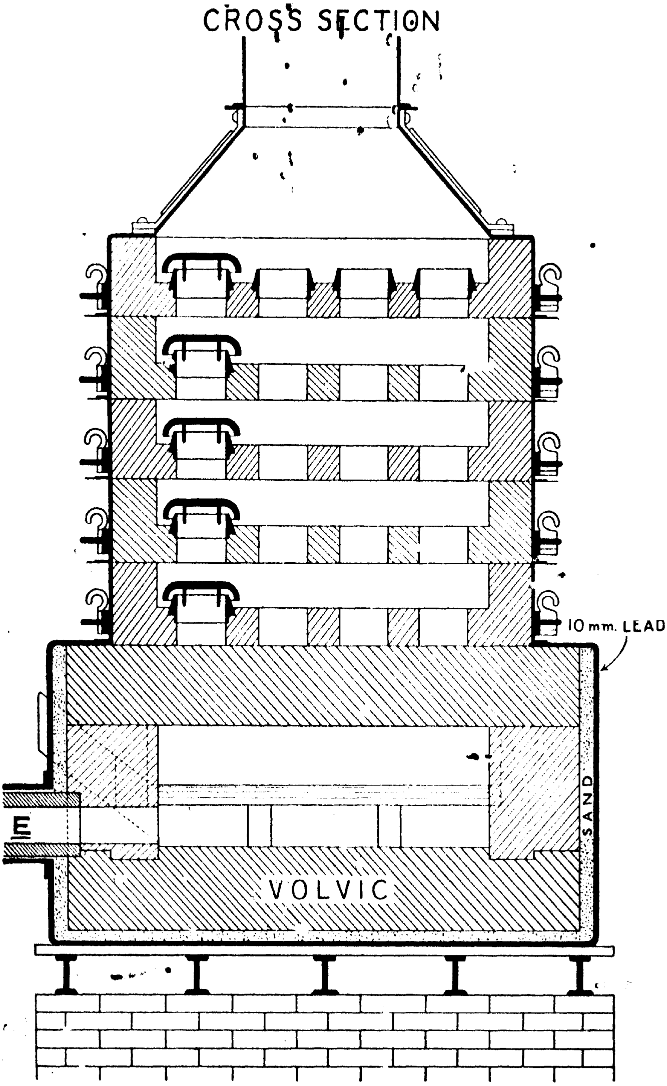


Fig. 87.

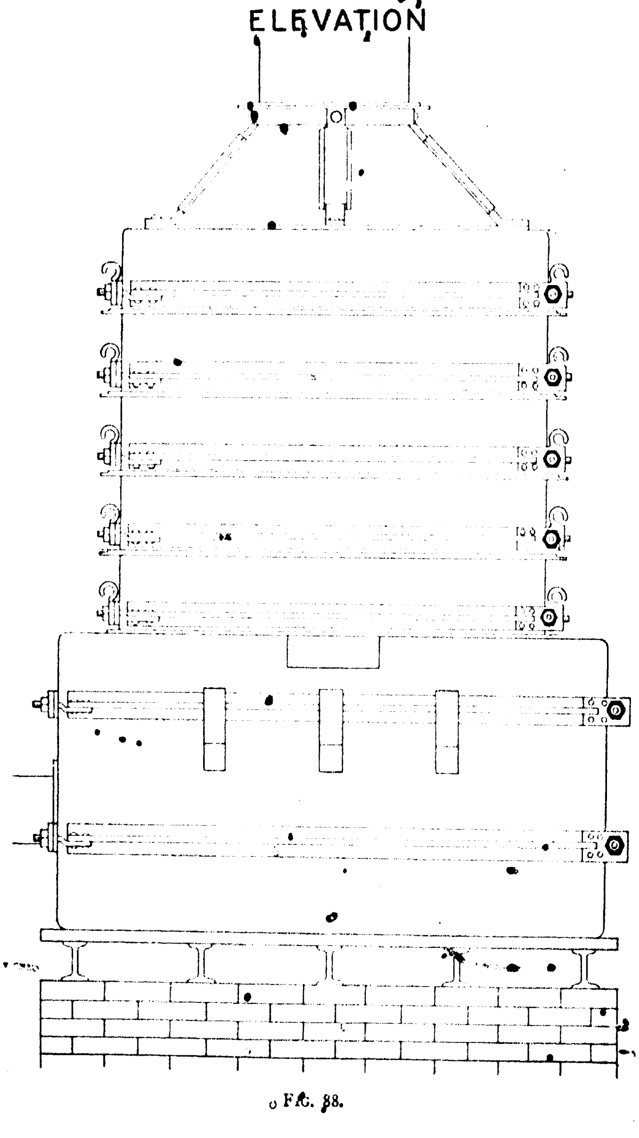


FIG. 38.

fastened on to joists carried across the width of the box. For protection against the cutting action of the coke, the bottom of the box and the sides to a height of 0·5 metre are lined with acid-resisting brick (about 2350 bricks, 220 × 110 × 55 mm. are required to protect the bottom and sides, and to support the grid). On the top of the bricks sixty-nine lead-covered round iron bars are placed, to form a grid for the support of the packing over the gas outlet (see drawing).

The coke for filling the condenser is the best hard steel coke, containing a minimum of iron, aluminium, chalk, and silica, and is graded as follows:—

	Quality.	Space occupied in Cubic metres.	Approximate Weight.
(1) Large pieces of 200 to 300 mm.	...	10,500	4,200 kg.
(2) " " 0·050 " 0·100 "	A	3,500	1,400 "
(3) " " 0·020 " 0·050 "	B	1,748	699 "
(4) " " 0·008 " 0·020 "	C	700	280 "
(5) " " 0·004 " 0·008 "	D	21,000	8,400 "
(6) " " 0·001 " 0·004 "	E	44,800	26,600 "

In order to obtain the 44,800 cubic metres of coke E, it is necessary to add 40 to 50 per cent. excess, which is lost as powder. All grades of coke should be free from dust.

Fan.—A 5-H.P., 12-in. high-pressure fan is made by the Kestner Evaporating & Engineering Co. of London, specially for the draughting of concentrating plants, and gives excellent service.

General Arrangement.—The general arrangement of the plant is shown in Figs. 80 to 82, from which it will be seen that the plant is a compact unit, housed in a building 11 metres long by 9 metres wide.

The apparatus is supplied in four different sizes.

Apparatus No. 1 will concentrate in twenty-four hours, 4 tons of 92 to 93 per cent. sulphuric acid from chamber acid of 113 to 116° Tw. Apparatus No. 2 will concentrate 6 tons of 92 to 93 per cent. acid under the same conditions. Apparatus No. 3 will concentrate 8 to 10 tons of 92 to 93 per cent. acid under the same conditions. Apparatus No. 3A will concentrate 12 to 15 tons of 92 to 93 per cent. acid under the same conditions. With the continuous producer these outputs can

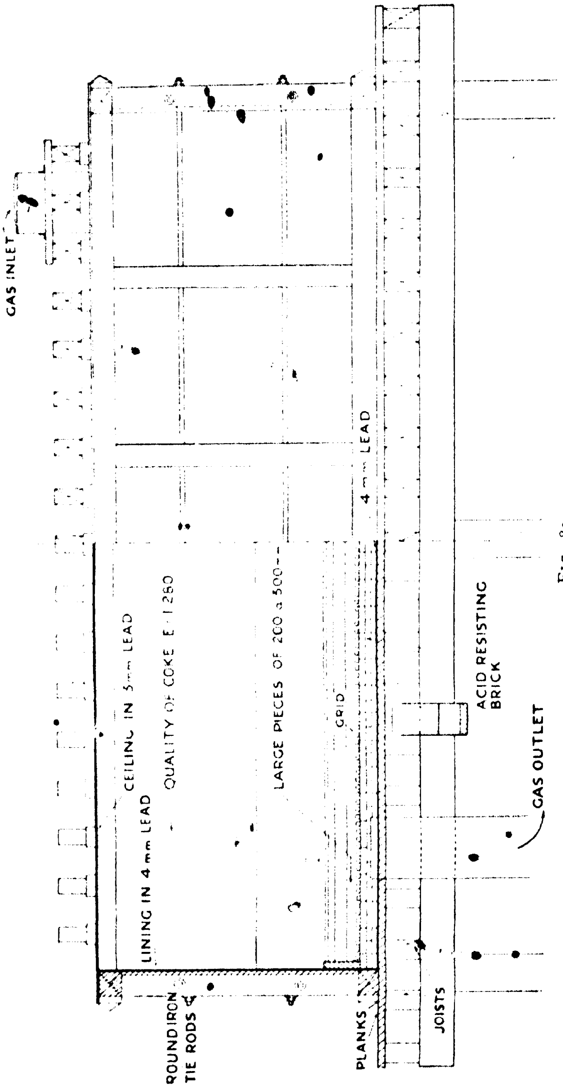

GAS INLET
CEILING IN 5 mm LEAD
QUALITY OF COKE E 1 250
LARGE PIECES OF 200 a 500
GRID
LINING IN 4 mm LEAD
4 mm LEAD
ROUNDIRON TIE RODS
PLANKS
JOISTS
ACID RESISTING BRICK
GAS OUTLET

FIG. 39.

be increased still further. As an example of the elasticity of the plant, it may be mentioned that, during the war, apparatus No. 3A, which produces normally 15 tons in twenty-four hours, actually produced more than 24 tons of 92·75 per cent. H_2SO_4 at one factory.

Kessler[1] defends his system against faults found with it by Hartmann and Benker. According to his Fr. Ps. 288752 and [illegible]05781, for the purpose of preventing the concentrated acid from acting upon the lead, it is made to flow through a heat-exchanging apparatus, in which the fresh acid cools the hot concentrated acid. (This has not been developed on a practical scale.)

In contradiction to a statement of Hartmann and Benker,[2] according to which Kessler's apparatus yields acid not exceeding 95 per cent. H_2SO_4, Gazel[3] asserts that the Kessler apparatus, supplied to the British Government in 1898, fulfils the condition laid down, according to which the acid must come up to a sp. gr. of 1·842 (95 to 96 per cent. H_2SO_4).

From a British factory he reports the following figures:—

Strength of feed acid	48° Bé. (100° Tw.)
Strength of concentrated acid . .	65·9 „ (168° T[illegible])
Production per day	9100 kg.
Coke used for the gas producer . .	650 „
Coal used for steam-raising . .	750 „

Luttgen[4] considers that the better effect of the new Kessler apparatus is due to the acid waves being formed by the hot gases passing through and impinging against the walls, so that both the effects of splashing and spraying are produced.

Stolzenwald[5] doubts the formation of spray in this case.

According to Luttgen (see above), the Kessler apparatus in its new form requires 80 to 100 kg. coke for producing 1 ton of acid of 92 to 93 per cent. H_2SO_4. The proportion of waste acid is very slight, and so is the cost of repairs. Acid of 98 to 99 per cent. H_2SO_4 is obtained with 180 to 190 kg. coke, and there is 200 kg. waste acid of 72° Tw. acid.

According to the 51*st Alkali Inspector's Report for* 1914, the Kessler system was being worked successfully, and more and more extending. The *52nd Report for* 1915 considers it one of the best existing.

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[1] *Monit. Scient.*, 1904, p. 557.

[2] *Monit. Scient.*, 1907, No. 782.

[3] *Ibid.*, 1907, p. 368.

[4] *Chem. Zeit.*, 1910, p. 24.

[6] *Z. angew. Chem.*, 1910, p. 1976.

According to Pohl,[1] vitreosil (fused silica ware) has advantages over the volvic lava employed in the Kessler plants. The latter is inclined to become tender, especially in plants worked intermittently; whilst vitreosil is not in the least damaged. Vitreosil pipes have much thinner walls than the lava pipes, but they are made with the same external dimensions, so that they can be put into existing plants without any alterations. The greatest difficulty in the working of the Kessler plant is the frequent breakage of the porcelain bells; instead of which, bells made of vitreosil are now employed of the shape shown in Fig. 89A, which fit to the lower parts in the existing apparatus. These are now provided with depressions, into which fit the opposite parts of the bells, so that they are placed always exactly over the centre of the lower parts.

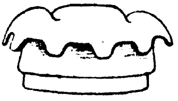

FIG. 89A.

The Working of a Kessler Plant.

The author is indebted to Mr W. G. MacKellar of The United Alkali Co., Ltd., St Rollox, Glasgow, for the following notes on the working of the Kessler plants, which were introduced into Glasgow as far back as 1894 at the works of Messrs Alex. Hope, jr., & Co., Ltd.

Gas Producer.—(1) Experiments have been made from time to time, with a view to working the gas producer continuously, but trouble has been experienced always, owing to the discoloration of the acid, which may be accounted for partially by the fact that anthracite is burned in the furnace instead of coke.

(2) The conditions for making 168° Tw. and 168·3° Tw. acid are much more exacting than when making 144° Tw. acid. When working at high strengths of acid, it is undesirable to produce any hydrogen, which would form water on combustion, and hence this condition negatives the use of a wet ashpit.

Saturex.—The saturex with transverse barriers is quite as efficient a concentrator as the old type with longitudinal ones, and the upkeep is very much less; probably only a quarter of the original. Three barriers instead of five, as originally supplied, are now used—one at the entrance of the producer gas, and two under the plateaux—the central two having been dispensed with. It is essential that the barriers do not dip into the acid, as this renders the apparatus unworkable. Violent pulsations take place in the whole body of the liquid, due to the hot gases alternately making and missing their way between the barriers and the acid; and the draught of the furnace is so impaired thereby that very poor results are obtained. The best results are obtained with only a thin film of acid, 1¼ in. deep on the bottom of the saturex.

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[1] *Z. angew. Chem.*, 1912, p. 1851.

Material made by the Accrington Brick and Tile Co., Ltd., Lancs., has been used for the cross barriers, and their supports, and all the small pieces necessary for the cleaning hole plugs. As it is impossible to get a material like this in slabs large enough to build a Kessler without an excessive number of joints, no attempts have been made to use sides or end stones or covers in any other material than volvic. (This experience does not agree with that obtained in another works, where transverse barriers in Accrington material gave much trouble through disintegration; on the other hand the material was found quite suitable for bottom or side stones, where, if cracking takes place, no harm is done owing to the lead covering. Furthermore, longitudinal barriers are more easily cleaned than the transverse type, and, if constructed in narki metal, are comparatively cheap, and last a long time. The transverse barriers, however, do not "muck up" so easily, which is an important point when dealing with an impure acid, particularly with waste nitration acid, so that, on the whole, the balance of experience is in their favour.) The run-off pipe is now made in vitreosil (fused silica ware). This pipe works under very exacting conditions; the end in the saturex is at a much higher temperature than the end in the cooler. Previously, when the cooler lid was lifted for examination, the inrush of cold air sometimes cracked the earthenware pipe, and a new pipe had to be fitted. The silica pipes are not so liable to break, owing to their low coefficient of expansion (see p. 110).

Recuperator.—The plateaux have been fitted with silica calottes and supports, with satisfactory results, especially in the three lowest plateaux. In connection with the acid level in the plateaux, it is essential that the calottes should only fit to half the depth of the scallop, otherwise the draught will be choked in the recuperator, and poor evaporation results will be obtained.

Condenser.—This is now built without any wood lagging and the coke in the bottom is laid transversely instead of vertically. The draught from the Kessler hood enters at the bottom of the box and leaves at the top.

Working Data.

Consumption of fuel in furnace per ton of 168·3° Tw. = 2·5 cwt.
" " " " 167·8° Tw. = 2·0 "
" " " " 144° Tw. = 1·12 "

Output per Twenty-four Hours.

(a) *Dearsenicated Acid*—

Feed acid 106° Tw., concentrated acid 168·3° Tw. = 10·80 tons.
" 106° Tw., " 144° Tw. = 20·00 "

(b) *Arsenical Acid*—

Feed acid 115° Tw., concentrated acid 167·8° Tw. = 15·00 tons.

Temperature of acid leaving saturex	245° C.
" on first plateau	210° C.
" of vapour leaving Kessler hood	125° C.
" of gases entering Kessler	750° C.
Corresponding CO_2	7·5 per cent.
Temperature of gases entering Kessler	710° C.
Corresponding CO_2	6·4 per cent.

H.P. consumption at fan, 5·5 E.H.P., and speed of fan, 1680 R.P.M. Fan placed outside of condenser box and delivering into chimney.

Water-gauge at fan entrance	7 in.
" Kessler hood	6½ "
" cooler top	1 "
Loss of head going through six plateaux	5½ "

Approximately 0·8 of an inch for each plateau.

Strength and weight of acid from condenser box at 80° Tw. per ton of 168·3° Tw. acid = 4·5 cwt.

Escape on 168·3° Tw. acid = 1·8 grs. SO_3 per cubic foot
" 144° Tw. " = 1·4 " " "

(The Kessler of the type recommended above and the working figures, while very suitable for making small quantities of high quality rectified oil of vitriol with good working efficiency, is out of date where big outputs are required, and unsuitable for working with dirty acid, or "spent" acid from nitration processes. In the latest modification of the Kessler type, the plateaux and calottes are abandoned altogether, and the recuperator constructed on the lines of the Glover tower, much as in the Gilchrist concentrator (see p. 239). English material is used exclusively for the construction of the plant, except in the saturex, and gives excellent results under these conditions. The output of such a unit with a large (14 ft. 6 in.) saturex is about 30 tons per day of 95 per cent. H_2SO_4, with a feed acid of 135° to 140° Tw., when fired with a continuous gas producer.

The Perrin Modification of the Kessler Plant.

Vialleix and Perrin[1] (B. P. 8142 of 1911; Fr. P. 420563; U.S. P. 1066557 of 1913) modify the Kessler apparatus by constructing the saturex of a single central channel and two side channels, through which the hot gases are aspirated. The "regenerator" is made to contain a number of superimposed hollow trays, arranged so that the acid overflows from one to another in a zigzag path; contact between the heated gases and the acid is secured by means of transverse ribs, which reach from the under surface of each tray to the level of the acid below; these ribs serving also to strengthen the trays. Lava or stoneware is used in the construction of the channels or trays, instead of the pumice and porcelain used hitherto.

Further improvements have been made by Perrin[2] (B. P. 118095 of 4th July 1919; U.S. P. 1301598), by the use of baffle plates in the flues, and dipping into the acid to form liquid seals, while the partitions between the flues extend downwards nearly to the surface of the acid, whereby the hot gases are constrained to flow repeatedly in a transverse direction from one flue to another during their passage along the flues. In the "regenerator," grooved instead of plain transverse ribs are employed. The apparatus is shown in Figs. 90 and 91.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1912, **31**, 187; *J. Soc. Chem. Ind.* (*Abstr.*), 1911, **30**, 360.

[2] *J. Soc. Chem. Ind.* (*Abstr.*), 1919, p. 629.

By means of a fan, the gases coming from the producer are drawn into the apparatus through the central flue (A); their progress towards the outlet is stopped by a baffle plate (B), which forces them to pass under each partition, and into the side flues, but even here the baffle plates (C and D) prevent them from continuing to follow their path, and force them to pass for the second time through the longitudinal

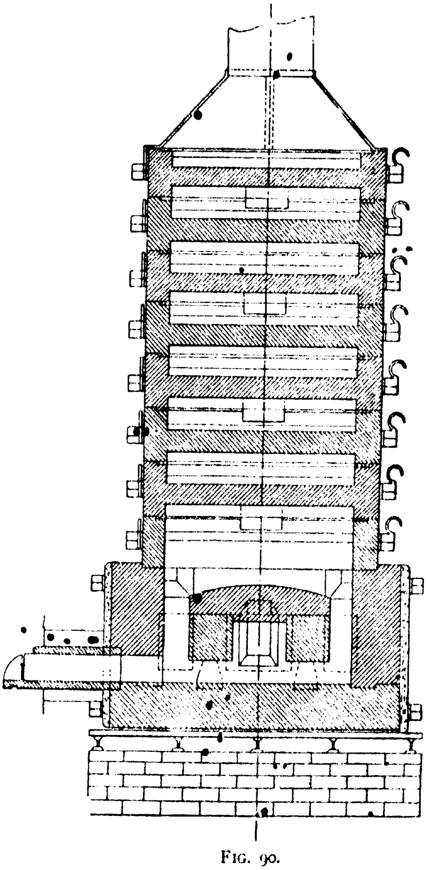

FIG. 90.

partitions, and so on. In Fig. 91 the arrows show clearly the path followed by the gases, which, from their admission to their escape from the saturator, remain in close contact with the acid to be concentrated. The baffle plates, B, C, D, project a few centimetres into the acid, so as to make a hydraulic joint; this ensures that the gases cannot circulate under the baffle plates, while they pass under the partitions. Port-holes are provided for the cleaning out of the saturator. On leaving the saturator, the hot gases are drawn into the regenerator, the troughs of which are provided with transverse ribs; the object of which is to keep back the gases, and to prevent them from circulating too quickly from a lower trough to an upper one. For the same reason, the projections are provided with a longitudinal V-shaped groove. Suitable cleaning holes are provided in the sides of the regenerator. 97 to 98 per cent. H_2SO_4 can be obtained with this apparatus.

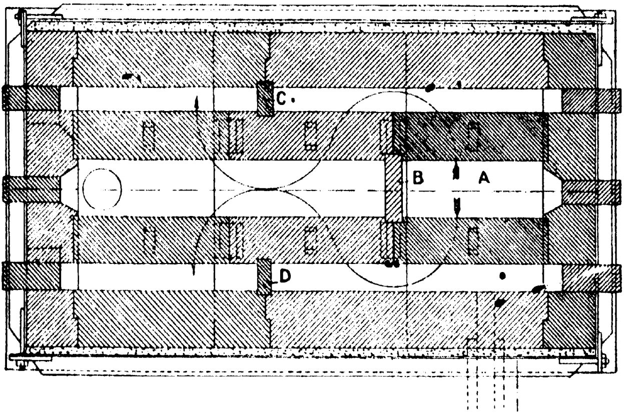

FIG. 91.

Figs. 92 and 93 show the layout of the plant as erected by Messrs J. F. Carmichael & Co., Ltd., of Liverpool. The plant will give an output of 6 tons per twenty-four hours of 97 per cent. H_2SO_4, from chamber acid of 1·58 sp. gr. (116° Tw.), using 14 tons of coke per 100 tons of concentrated acid produced.

In a private communication to the author, Mr C. S. Imison of the United Alkali Co., Ltd., Widnes, states that concentrators of the Perrin type gave satisfactory results during war-time. The advantage of this type of plateau was that its construction in English-made acid-resisting material presented far less difficulty than that of the Kessler plateau, with its elaborate up-stands and calottes. The output, however, was never quite as good as that of the Kessler, and the loss somewhat higher. Material made by Messrs Davison

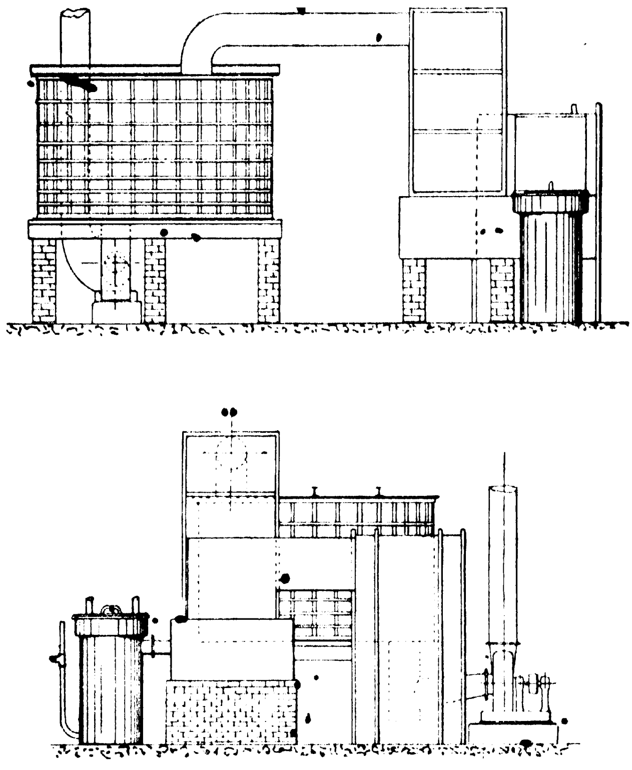

FIG. 92.

of Chester, and The Accrington Brick & Tile Co. proved fairly satisfactory, and gave little trouble when the plant was kept in continuous operation; long stoppages, however, afterwards caused trouble through disintegration, from which volvic stone is much more free.

Viaillieux and Perrin (B. P. 28302 of 1909; Fr. P. 397080) facilitate the condensation of the vapours arising in the concentration of sulphuric acid, by embedding in the coke used for this purpose, coils in which cold water or acid circulates, or by moistening the coke.

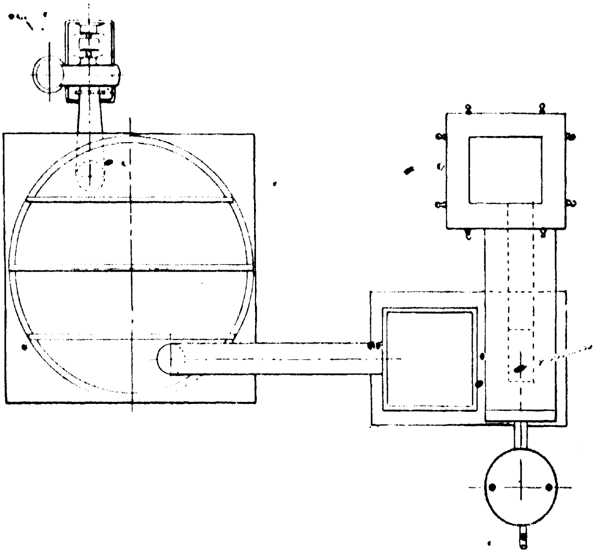

FIG. 93.

Moss[1] describes a modified Kessler with open type plateaux. The saturex and plateaux are constructed of vitrified earthenware blocks, the joints being made with special cement. The coke consumption is about 19 per cent.

The author is indebted to Mr J. Rogers, Technical Manager, Nobel Industries, Ltd., for the following information on the working of the Kessler plants at Rembrey (1915 to 1918).

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1918, p. 72.

The units were all of what is known as the "medium size," the output of which may be taken as in the neighbourhood of 8 tons per day, concentrating from about 66 per cent. to 93 per cent. H_2SO_4. The output varied, of course, according to the strength of the acid treated and of the acid produced. The units embodied all the latest improvements at the date of their erection. Both the Kessler and Perrin types were used, and in addition the experiment was tried of combining both types of plateau in a single unit, the six upper plateaux being of the Kessler type, and the two lower, of the Perrin type. Modifications of the baffling arrangements in the saturex were also tried. In one unit, one central transverse baffle only was built, and this was arched considerably, so as to allow the gases to pass easily, but at the same time to produce a mixing effect. Another unit was built with no baffles whatever, to test a view advanced that the baffles are of little value. It cannot really be said that any one, or even any combination of these ideas, gave what might be considered as a final standard type of plant. Attempts were also made to find a substitute for volvic stone, chemical ware being tried for this purpose. The results showed, however, that, with its drawbacks, volvic stone was still the more satisfactory material. The calottes in chemical ware were especially found to deteriorate rapidly.

The following results were obtained on a seven days' comparative test of a Kessler and of a Perrin Unit, and, while on account of the shortness of the period of test they cannot be accepted as conclusive, they serve to illustrate the course of ordinary good working:—

Working Data.

	KESSLER.[1]	PERRIN.
Speed of fan	1510 revs. per min.	1010 revs. per min.
Speed of exit gases	21·5 ft. per sec.	11·5 ft. per sec.
SO_3 in exit gases	2·8 grains per cub. ft.	3·0 grains per cub. ft.
Temperature at top of recuperator	80°-105° C.	110°-120° C.

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[1] The Kessler used in the test was that containing two Perrin plateaux.

General.

	Kessler.			Perrin.		
	Strength.	Acid.	H_2SO_4.	Strength.	Acid.	H_2SO_4.
	Per Cent.	Tons.	Tons.	Per Cent.	Tons.	Tons.
Strong acid produced.	92·7	56·47	52·34	92·0	43·76	40·26
Condenser acid . .	62·20	7·31	4·50	62·73	6·78	4·25
Fan acid . . .	38·5	1·36	0·52	25·1	1·36	0·34
Exit losses . .	...	...	2·16	...	...	1·20
Fuel consumed . .	4·35 tons			3·3 tons		
Fuel consumed per ton H_2SO_4 produced	0·083 ,,			0·082 ,,		

In general, it was found that all the variations of the types of plant gave satisfactory service. At the same time Pembrey's experience was that the Perrin Plant had a somewhat smaller capacity than the Kessler, the ratio being as 4 : 5. On the other hand, the simpler construction of the Perrin plateau is a point in its favour, especially when dirty acid has to be concentrated. The Kessler plateau is more difficult to clean, and the calottes are easily damaged, thus adding, of course, to maintenance charges.

The Duron Modification of the Kessler Plant.

Duron[1] (B. P. 344 of 1913; Ger. Ps. 257559, 257573; Fr. Ps. 453733, 453742) modifies the Kessler apparatus as follows.

The heating gases are conducted in parallel branches, perpendicularly to the direction of the current of acid, over the top of this, thus exposing the acid several times to the action of the hot gases. Two gas-flues are arranged at the longitudinal sides of the concentrator, and are connected by transverse channels, which are connected in turn with the entrance and exit-flue. The floor of the concentrator is divided into three longitudinal channels, along which the acid from a regenerator column flows in a zigzag path in the opposite direction to the heating gases.

Duron[2] quotes the results of working his apparatus for producing concentrated sulphuric acid of various strengths up to monohydrate acid. He claims for his apparatus the special advantages of doing away with distilling acid, lead pans, acid vapours, of a specially efficient gas producer, and of considerably lower cost than either the Kessler or Gaillard apparatus.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1914, p. 790.   [2] *Chem. Zeit.*, 1914, p. 559.

The latest modification of the Duron system is given by B. P. 104034 of 24th February 1916.[1]

By leading the hot gases through horizontal flues placed directly over three parallel channels containing acid to be concentrated before passing over the surface of the acid in the reverse direction, the hot gases are caused to give up their excess of heat to the gases actually effecting the evaporation of the water from the sulphuric acid. By this means the dissociation of the acid by the hot gases is reduced to a minimum. The concentration is effected in stages, in separate parallel channels, in which the currents of gas producing the evaporation pass simultaneously; and of which the relative dimensions are in proportion to the quantity of water to be evaporated in each of them, and to the difficulties of evaporation. The apparatus is shown in Fig. 94.

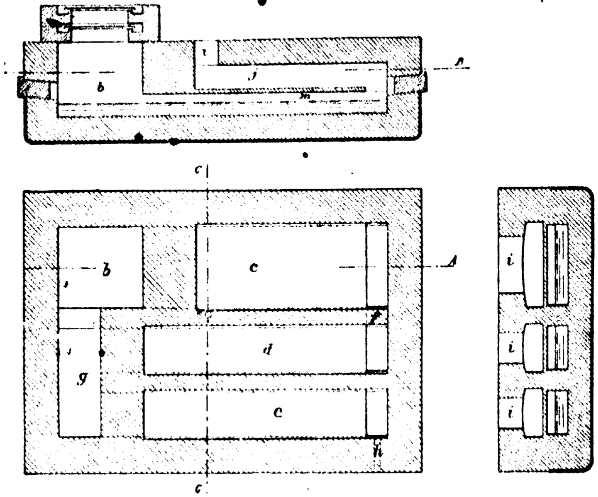

FIG. 94.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1917, p. 385.

The path which the acid to be concentrated travels in the concentrator is along *b*, *c*, *f*, *d*, *g*, *e*, and *h*, where *b* is the inlet and *h* the outlet. The gases, entering at a high temperature through the inlets *i* into the flues *j*, heat the partitions, and after their temperature has been lowered by this work to a point below which dissociation of the acid does not occur, the gases come in the spaces *m* directly in contact with the acid, where, by reason of their temperature and dryness, they effect the evaporation of the water. This evaporation of the water tends to lower the temperature of the gases, and hence to reduce their evaporating power; but the temperature is maintained by the contact with the heated under-surface of the partitions *n*, which have been raised to a high temperature by the in-coming furnace gases.

The re-heating of the evaporating gases is greatest at the point of exit, where the reduction of temperature would be greatest otherwise. The concentration of the acid is effected in progressive stages, by means of the arrangement of separate channels, heated simultaneously. With feed acid of 65 to 67 per cent. H_2SO_4, the acid enters the concentrator from the "regenerator" column increased to 70 to 76 per cent. according to the final degree of concentration.

	Per cent.	
In channel *c* the degree of concentration is raised to	72-90	H_2SO_4.
" *d* " " "	88-96	"
" *e* " " "	92-98·3	"

The plant shown in Fig. 94 is built entirely of volvic stone and acid-resisting metal, without any porcelain parts, in five different sizes, up to 30,000 kg., 92 to 93 per cent. H_2SO_4 per twenty-four hours, and can be adapted for heating with coke coal, peat, oil, and tar.

The following figures are quoted in a recent trade circular:—

Concentration up to 66° Bé. (92 to 93 per cent. H_2SO_4).

	Model III.	Model IV.
Acid at inlet	116° Tw.	116° Tw.
Consumption of fuel	6·8 per cent. coke	3·5 per cent. tar
Horse-power consumed	2·4 H.P.	2·9 H.P.
Production in 24 hours of 92·5 to 93 per cent. H_2SO_4	12,500 kg.	21,700 kg.

Concentration up to 97 to 98 per cent. H_2SO_4.

	Model III.
Acid at inlet	116° Tw.
Consumption of fuel	13 per cent. coke
Horse-power consumed	2·5 H.P.
Production in 24 hours of 97·5 to 98·3 per cent. H_2SO_4	5300 kg.

Efficiency Data for the Kessler Plant.

The following figures on the concentration of sulphuric acid by the Kessler system are abstracted from the Report on the Statistical Work of the Factories Branch of the Department of Explosives Supply, Ministry of Munitions:—

H.M. FACTORY, PEMBREY. Week ending 6 A.M., 2nd February 1918.

Sheet B2. Concentration Kessler.

	T.N.T. Waste Acid.			B.O.V. and N/G and N/C Waste Acid.		
Number of units working		14			7	
Number of unit-days worked		974			48	
Weak acid charged		1111·1	tons		711·5	tons
Containing H_2SO_4	66·33 %	737·0	,,	77·11 %	548·6	,,
Strong acid produced	...	765·5	,,	...	582·1	,,
Containing H_2SO_4	91·75 %	702·4	,,	90·98 %	529·6	,,
H_2SO_4 lost	...	34·6	,,	...	19·0	,,
Loss as percentage of H_2SO_4 in weak acid charged		4·7 %			3·5 %	
Fuel consumed	Coal	63·4	,,	Coal	26·9	,,
	Coke	28·1	,,	Coke	16·9	,,
Fuel consumed per ton of H_2SO_4 in strong acid produced	Coal	0·09	,,	Coal	0·05	,,
	Coke	0·04	,,	Coke	0·03	,,

CONCENTRATION OF SULPHURIC ACID IN THE GAILLARD TOWER.

Gaillard[1] (B. P. 23841 of 1905; B. P. 12538 of 1906; U.S. Ps. 856048, 859757, and 859759; Ger. Ps. 192153 and 205912; Fr. Ps. 359442, 367376, and 390807) introduced an entirely new principle in the atomising of the acid to be concentrated, in the form of a fine spray down an empty tower, up which hot gases from a coke producer are ascending. Under these conditions, the contact between the acid and the hot gases is as intimate as possible, and evaporation takes place regularly throughout the tower, so that the acid arrives at the bottom of the apparatus in a highly concentrated condition, and the gases, which enter the base at a red heat, are reduced considerably in temperature when they leave the top of the tower. The concentration takes place quite independent of any special design of the plant, and the tower acts merely as a sort of passage or flue for the hot gases and acid fumes to travel. There is, therefore, very little to break or get out of order, and the life of the tower depends entirely on the acid-resisting qualities of the material of which it is constructed.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1906, p. 638; *J. Soc. Chem. Ind.*, 1907, p. 201.

The earliest plants which Gaillard erected consisted essentially of a gas producer, a tower, a scrubber, and a fan; but it was realised very quickly that some form of recuperator was necessary, and a small tower, similar in shape to the main tower, was introduced into the system in front of the scrubber. Weak acid was atomised down this tower in the same way as in the main tower, and slight preliminary concentration of the acid effected. At the same time the temperature of the gases leaving the recuperator was reduced to such a degree that they could be forwarded safely to the coke scrubber.

Recke[1] gives particulars of the plant outlined above. The producer is charged with coke, and is 3 metres high, 4 metres long, and 2·8 metres wide. The main concentrating tower is 15·5 metres high, and consists of fifteen volvic rings, superimposed over one another, without any mortar or cement. Each ring consists of eight lava blocks, held together by lead-covered iron rings. The blocks have V-shaped longitudinal grooves, so that, at the junction of each two blocks a channel is formed, which is filled with a cement of volvic powder and sodium silicate. The tower at the bottom has an internal diameter of 1·70, and at the top 2·0 metres; the thickness of the walls is 450 mm. at the bottom rings, 400 mm. at the fourth rings, 250 mm. at the three following rings, 200 mm. at the three following and 150 mm. at the four top rings. The top of the tower is formed of four volvic plates, with an inlet for the spray nozzles, and a 500 mm outlet for the waste gases. The bottom of the tower is formed by a tray 400 mm. high, with twelve outlets for the hot strong acid, which is cooled by a tubular cooler, 80 metres long, placed in the bottom tray round the tower. The recuperator tower is made of 4 mm. lead, lined with 80 mm. stoneware plates, and held together by a frame of wood and iron. It is 8 to 10 metres high, 1·51 metres wide outside, 1·34 metres inside. It is placed on a wooden or iron frame, at such a height that its top is at the same level as that of the main tower. It has two spray nozzles at the top, and an outlet for acid at the bottom, and is connected with the top of the main tower by a volvic or stoneware pipe, 500 mm. wide, descending from the latter and entering it near the bottom. From the top of the recuperator, the gases pass through a coke filter, which consists of a wooden box lined with 3 mm. lead, 3 metres high,

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[1] *Chem. Zeit.*, 1910, pp. 173 and 182.

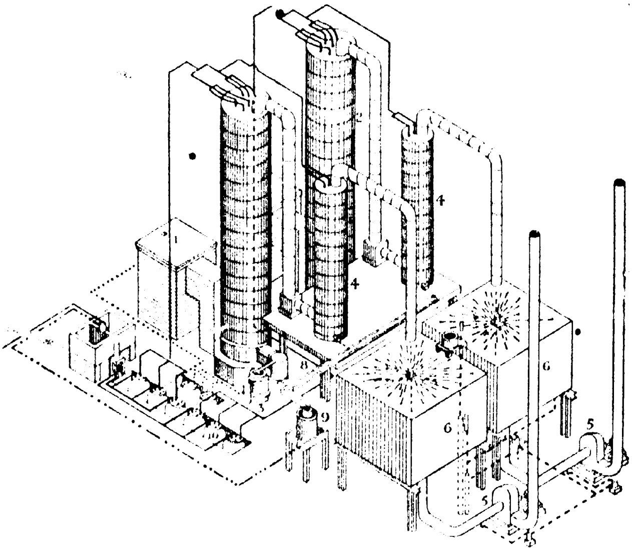

FIG. 95.

7 metres long, and 5 metres wide. The gases enter at the top and leave at the bottom. The coke rests on a grate of acid-proof bricks, and is graduated in size from 60 to 100 mm. at the bottom to 15 mm. at the top. The gases are drawn through the plant by means of a fan.

The plant is worked as follows: The gas producer is charged every two or three hours with coke of 40 mm. size, which should be dry and free from non-coked coal, which would impart a brown colour to the acid. The gas meets secondary air preheated by a firebrick grating, and the flame enters the base of the tower, where it meets the acid converted into a fine spray by means of a nozzle and compressed air. The concentrated gas flows through a cooler in the bottom tray. The gases leave the tower at its top, and enter the recuperator tower at a temperature of 200° C., where the acid mist is retained partially by the weak acid falling down the tower. The uncondensed gases pass then into the coke scrubber, through the fan, and out into the atmosphere.

Stolzenwald[1] states that the life of the plant is about six years, and that the acid requires to be filtered carefully in order not to choke the spray nozzles. This is also pointed out by Lüttgen.[2]

Lowy and Klagsbrunn (Aust. P. appl. A6792 of 1909) in the case of acids forming crusts of ferric sulphate, collect the hot acid in an acid-proof dish, from which it runs into an outside settler.

J. W. Parkes and E. G. Coleman[3] describe the development of the Gaillard concentration plant.

A plant of similar design to that described above was erected in 1908 at Messrs Kynoch, Ltd., Explosives Factory, Arklow, Co. Wicklow, and produced an average of 50 to 60 tons of 95 per cent. H_2SO_4 from a feed acid of 68 to 70 per cent., with a fuel consumption of 14 to 15 per cent. of the weight of finished acid. The fume from the hot acid in the basin was an objectionable feature of the plant, and the cooling system was difficult to maintain in an efficient condition, as the pipes became covered rapidly with mud. The port-holes for the outlet of the acid into the basin silted up

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[1] *Z. angew. Chem.*, 1910, p. 1976.

[2] *Chem. Zeit.*, 1910, p. 23.

[3] *J. Soc. Chem. Ind. (Trans.)*, 1920, p. 257.

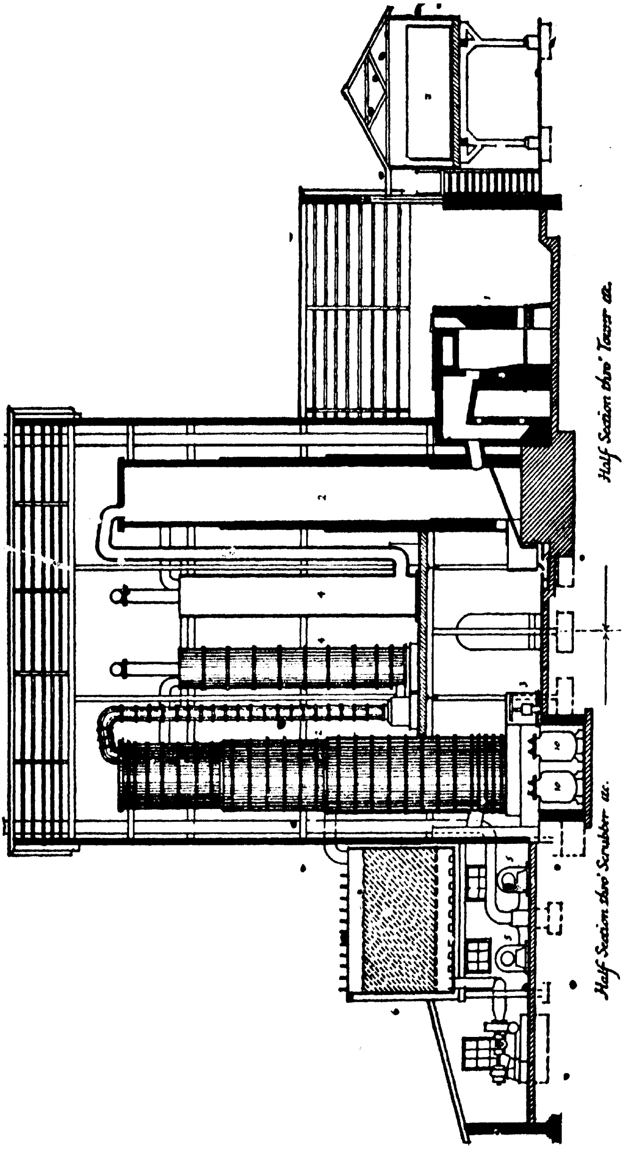

FIG. 96.

frequently, and when the inside of the tower base became choked with sludge, it was necessary to close down the entire plant and clean out the mud from the inside of the tower, the only entrance to which was through the gas flue from the producer.

The first Gaillard tower built entirely of acid-resisting blocks (obsidianite) was erected in Natal by the same firm in 1911, and a most important improvement was carried out also at this time by the installation of a sloping base inside the tower, and the introduction of a sealed mud settling tank and cooler. By this means fume from the base of the tower was prevented, and the sludge deposited was trapped by the mud-catcher, and washed out through the sludge pipe fixed in the bottom; whilst any collecting in the tower bottom was removed readily by means of a rake through an opening provided for the purpose in the wall of the tower (see Fig. 100).

A short description of the plant as worked at Arklow (1915-1918) is given below.

Gas Producer for Gaillard Tower.

The gas producer is shown in Figs. 97, 98, and 99, and has a combustion chamber 4 ft. 3 in. square by 7 ft. 6 in. high above the fire-bars. The grate is formed of fifteen wrought-iron bars, 1⅝ in. square, which are rounded to rest and turn on grooved cast-iron bearer bars, and extend through the back wall of the furnace, to facilitate their being turned by means of a key similar to that used on pyrites burners. A charging hole, 14 in. by 12 in., communicating with the combustion chamber, is formed in the top of the producer, and is sealed by means of a heavy armoured firebrick slab. Outside the firebrick lining of the combustion chamber, the shell of the producer is pierced by a series of channels through which the secondary air passes. By this means the air is heated before mixing with the producer gas in the entrance flue to the main tower, and at the same time acts as an insulator. The coke is weighed in quantities of 1 cwt. in wire baskets, and elevated to the producer top by means of a pneumatic hoist, where it is dried by the radiant heat before charging. When the furnace is ready for charging, 12 cwt. of coke is tipped from the baskets through the charging hole, and the opening sealed again. This is carried out every six hours, and the bars are turned every two hours to shake up the fire and remove the ashes.

In a recent design of plant, a producer having two combustion chambers, charged alternately, has been adopted. A

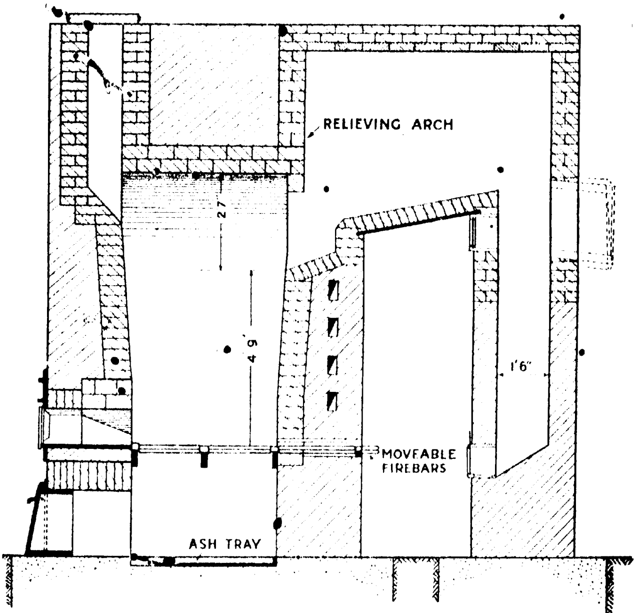

FIG. 97.

charge consisting of 75 per cent. anthracite and 25 per cent. coke has been worked successfully on both the single and double furnaces.

Main Gaillard Tower.

The tower is erected inside a dish formed of 30-lb. sheet lead on a concrete block, standing about 3 ft. 3 in. above the floor level. The floor of the dish is protected by a layer of

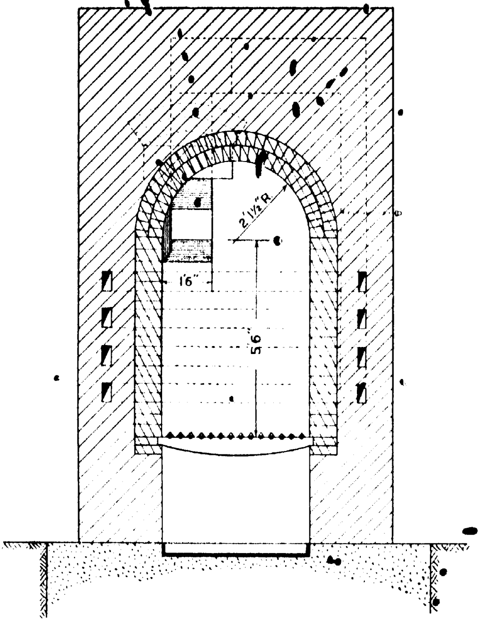

FIG. 98.

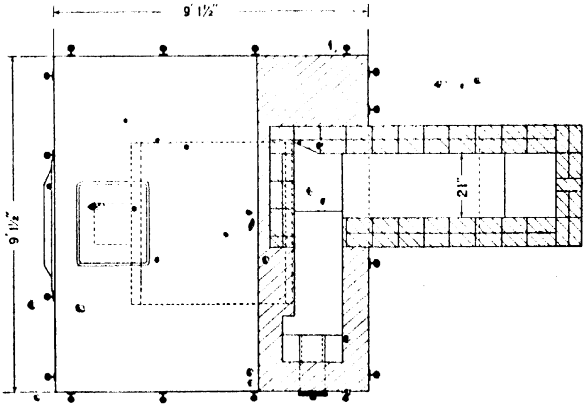

FIG. 99.

4 in. obsidianite slabs set in acid-resisting cement. On this floor, the curved blocks, 24 in. by 5½ in. thick, and of varying widths, forming the shell of the tower, are erected and properly jointed with an acid-proof cement consisting of finely-ground obsidianite or lava de volvic and silicate of soda solution, great care being taken to ensure that the joints and cavities in the rings of blocks are properly filled and consolidated with the cement. The blocks are laid so as to break joint, as in brickwork. Up to a height of 10 ft. 6 in. above the floor of the tower the shell is built, five blocks thick, at which point the inner ring, which serves the purpose of protecting the main blocks from the hot gases, is discontinued, and at a height of 24 ft. above the base the outer ring is discontinued. The shell is comprised of three blocks in thickness, up to a height of 36 ft. 6 in. above the base; and from this point is continued, two blocks in thickness, to the top of the tower—a total height of 48 ft. The internal diameter of the tower is 6 ft., except for the height of the protecting ring, which is 5 ft. 6 in. diameter. Each tier is secured by lead-covered iron bands. The gas inlet flue enters the shell at a height of 5 ft. 6 in. above the base—the latter being built up to form an incline from a point 6 in. below the gas inlet to the level of the base tiles at the acid exit from the tower.

The tower is surmounted with a volvic stone top, 9 in. thick, in four sections, held together by iron bands. The top is pierced with six atomiser apertures, and also for the gas outlet pipe. The gas pipe (18 in. diameter), which conveys the gases from the top of the main tower to the foot of the recuperator, is constructed of curved obsidianite tiles, 1½ in. thick by 12 in. high, and covered with 9-lb. sheet lead bands, and supported by a timber frame, and erected on a block of volvic stone in which the bend connecting to the recuperator is formed. This block bend is covered with 9-lb. sheet lead, and set in a lead saucer on the recuperator floor level.

Recuperator.

The recuperator tower is erected on a platform 15 ft. above the ground floor of the plant. The tower (29 ft. high by 4 ft.

6 in. internal diameter) is built of one thickness, of obsidianite blocks, 3¼ in. thick by 24 in. by 15¾ in., jointed and set in acid-resisting cement, and covered with 9-lb. sheet lead, and erected inside a 14-lb. sheet lead saucer. The cover of the tower is formed of 14-lb. sheet lead, supported by lead-covered iron

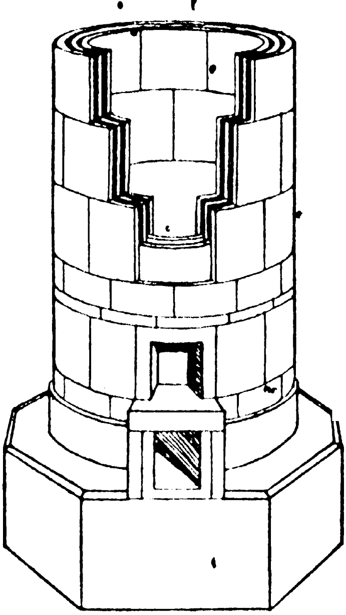

FIG. 100.

bars, and is pierced by two atomiser apertures, and by an 18-in. gas outlet pipe. Under normal working conditions, there are two sprays atomising the acid down the recuperator, and the acid overflowing from the foot at a temperature of 150° to 160° C. runs through a cooler, to reduce its temperature to 50° to 60° C., before passing to the feed tanks for use on the main tower.

Scrubber.

From the recuperator tower the gas passes to the top of the scrubber, which consists of a lead-lined box, 16 ft. 5 in. square by 13 ft. high (internal dimensions). The box is sheeted half way up the sides with timber, and lined with 14-lb. sheet lead. The bottom of the scrubber is paved with 1½-in. bricks, on which is built a series of brick channels, covered with spaced tiles, on which the packing is placed. The coke used is the very best hard steel coke, free from iron and other impurities. A foundation is formed with a layer of 12-in. coke, to support the main packing, which consists of pieces of coke graded uniformly from 3-in. to ½-in. pieces, covered with a thin layer of very fine coke free from dust. The condensed acid runs from the bottom of the box, through a cooler, to a Pohle air lift, and is elevated by this means to a small distributing box (18 in. diameter by 18 in. deep) on the top of the scrubbers connected to automatic flush siphons feeding luted or sealed distributors on the top of each scrubber. By means of this system of circulating the scrubber acid, the coke is cooled and moistened, and the acid raised in strength to 90° to 100° Tw.

Fan.

The draught through the system is produced by means of a 16-in. Kestner high-pressure fan, direct-coupled to a 10-B.H.P. motor with a variable speed control of 900 to 1700 revolutions per minute.

The following manometer readings are typical of the resistances offered:—

	Manometer Reading.	Resistance.
At inlet to main tower	− 0·6	...
At outlet from main tower	− 1·1	0·5
At top of recuperator	− 1·9	0·8
At inlet to scrubber	− 3·0	1·1
At inlet to fan	− 4·5	1·5
At exit	+ 0·1	...

The gas is expelled from the fan into an 18-in. exhaust pipe, which is carried up through the roof inside the main tower building, and discharges into the atmosphere. The centrifugal motion imparted by the fan to the gas effects a further condensation of the acid mist escaping through the scrubber, and the condensed acid (66° to 70° Tw.) runs away to a central receiving box.

Acid Circulation.

Each tower is supplied by three vertical cast-iron eggs (each 3 ft. 9 in. internal diameter by 5 ft. 6 in. total height), which are connected with the atomisers at the top of the tower and its recuperator, by means of a 1-in. extra heavy lead pipe, through which the acid is blown by compressed air at 80 to 85 lb. pressure. Each egg is worked in turn, and is not blown completely empty, so that any mud or sediment will remain at the bottom, and not tend to block the pipes and atomisers. As an additional precaution, two grit traps are inserted in the pipe line at the tower top, Fig. 101. The atomiser is made in regulus metal, of a composition of about 88 parts lead and 12 parts antimony, and comprises three essential parts—viz., the body (A), cap (B), and spiral centre (C). The extension on the under side of the cap terminates in a cone-

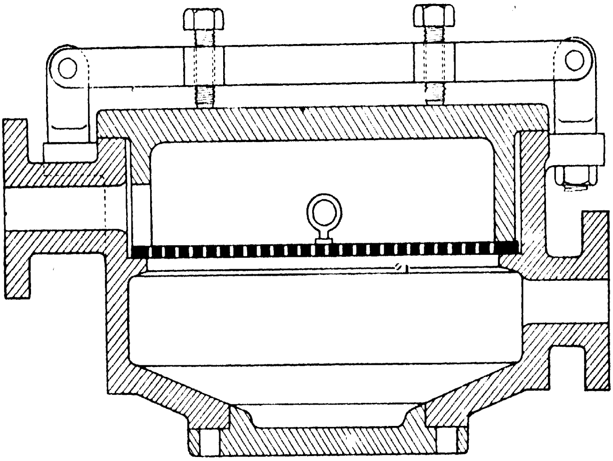

FIG. 101.

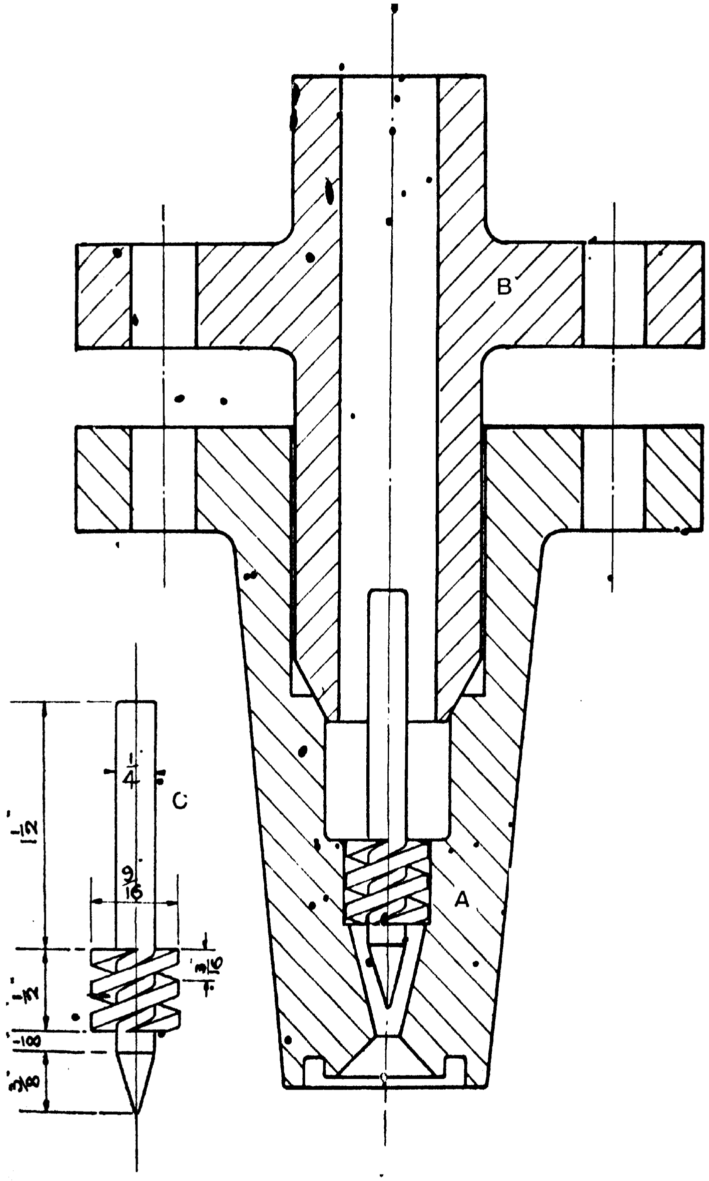

FIG. 102.

making joint, with the seating in the body (A), to which it is secured by means of bolts. The spiral centre is essentially a double-threaded worm, with a two start square thread of ⅜-in. pitch, having an extended stem to facilitate removal. The acid is forced through the atomiser by compressed air, and given a rapid rotating motion by the spiral centre, and expelled through the outlet in a uniformly fine spray in the form of a hollow cone. The concentrated acid falling to the base of the tower runs into a mud-catcher, and thence into a cooler. The mud-catcher is formed by an extension of the 30-lb. lead saucer of the tower in the shape of a cylindrical tank, the wall of which is lined with obsidianite tiles 2 in. thick, set in acid-resisting cement, having an internal diameter of 3 ft. 2 in., and a depth of 2 ft. 3 in. It is fitted with a detachable steel cover, and a 4-in. outlet pipe for the removal of the mud. The inclined base of the main tower is extended through an opening formed in the tower wall to the edge of the mud-catcher. To rake out the mud deposited on the inside of the tower base, the plant is shut down, and a special movable block above the outlet removed. A rake is then inserted through the opening, and the sludge pulled into the mud-catcher. At a height of 34 in. above the base of the mud-catcher, the acid runs through a T-pipe, which dips into a cooler. This is a cast-iron cylindrical vessel (3 ft. 2 in. internal diameter by 3 ft. 11 in. deep) fitted with a mild steel water-jacket. The water is cooled by means of two coils, each 3 ft. 5 in. high, and made of sixteen turns of 1¼ in. by 16 lb. per yard lead pipe: one 3 ft. in diameter, and the other 2 ft. 6 in. in diameter. The cooling water runs through the two coils in parallel, and then discharges into the outer jacket. The concentrated acid from the cooler flows into eggs, from which it is blown to the storage tanks.

Output of Gaillard Tower.

The output varies according to the strength of feed acid supplied, and to the degree of concentration of the finished acid. With a feed acid of 70 per cent. H_2SO_4, the tower concentrates 30 tons per twenty-four hours up to a strength of 95·5 per cent H_2SO_4. The output increases rapidly as the strength of the finished acid falls, and the tower will produce 40 tons per twenty-four hours of 92 to 93 per cent. H_2SO_4.

The approximate temperatures at the various points of the system are as follows:—

Furnace	1000	to	1100° C.
Mixing chamber	850	„	900° C.
Entering tower	750	„	800° C.
Recuperator	195	„	205° C.
Scrubber	100	„	120° C.
Fan	60	„	70° C.

The chief guide to the working of the plant is the temperature of the gases entering the recuperator; and, to facilitate the controlling of the plant, this temperature is recorded by means of a pyrometer fixed in a convenient position on the ground level. If the temperature rises, there are two courses to adopt: (1) increase the flow of acid down the main tower by bringing into use larger or additional atomisers; (2) increase the volume of secondary air. As a further guide to the working of the plant, the strength of acid leaving the coolers is recorded hourly.

Kaltenbach[1] states that a standard tower, 3 metres internal diameter, will produce about 52 tons of 93 per cent. acid per twenty-four hours, with a coke consumption of 10 per cent. The gases from the producer enter the main tower at a temperature of about 850°, and leave it at 200 to 220°.

For satisfactory work, the gases should leave the recuperator at a temperature just above their saturation point—say, 120 to 130°.

The Gaillard Plant at Queen's Ferry.

A very valuable and interesting monograph on the concentration of sulphuric acid, with special reference to the Gaillard concentrators, at H.M. Factories, Gretna and Queen's Ferry, has been published by the Ministry of Munitions and Department of Scientific and Industrial Research (*Technical Records of Explosives Supplies*, No. 3), from which the following facts are taken. The concentration plant at Queen's Ferry consists of two batteries of eight towers each, complete with all

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[1] *Chemie et Industrie*, 1921, p. 143; *J. Soc. Chem. Ind.* (*Abst.*), 1921, p. 256.

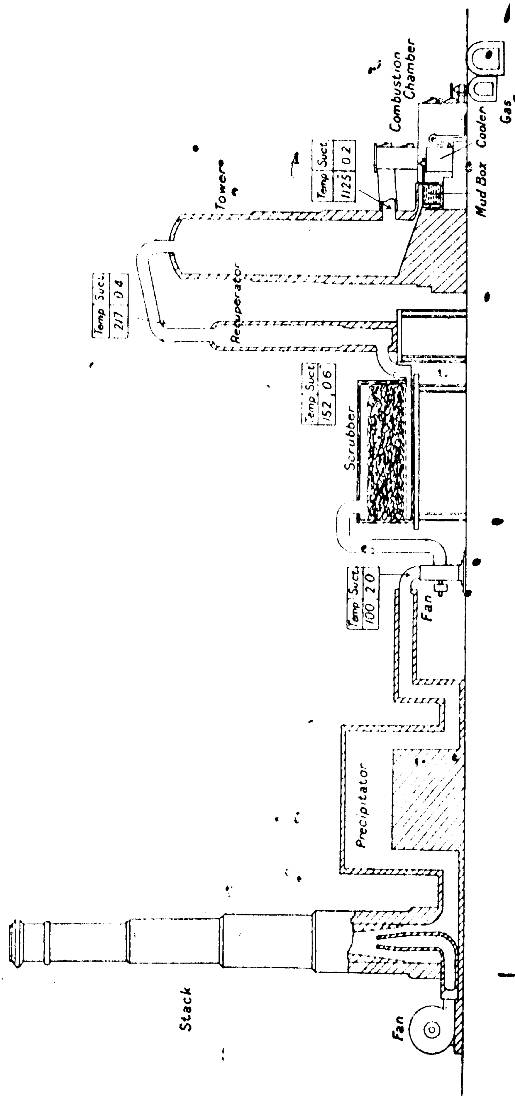
Combustion Chamber
Gas Flues
Cooler
Mud Box
Temp Suct.
1125 0.2
Tower
Recuperator
Temp Suct.
217 0.4
Temp Suct.
152 0.6
Scrubber
Temp Suct.
100 2.0
Fan
Precipitator
Stack
Fan

FIG. 103.

the necessary furnaces, recuperators, scrubbers, feed tanks, etc. The general arrangement of one of the units is shown in Fig. 103.

Furnace.—The producer gas is supplied from a central gas-producing plant, through a brick-lined flue (3 ft. by 4 ft.), into an iron-cased combustion chamber (5 ft. 6 in. by 6 ft. by 4 ft.). Primary air is delivered through a brick chequer into the front of the furnace, and secondary air is admitted through a separate opening on either side to the top of the furnace. The producer gas is burned with an excess of secondary air, and the hot gases pass through a brick flue (27 in. diameter) into the base of the main tower.

Main Tower.—The tower is 47 ft. 6 in. in height from the base to the springing of the curved top, and is built of joggle jointed acid-proof bricks in rings, each 3 in. thick, bound together by lead-covered mild steel hoops spaced 20 in. apart, with an internal diameter of 8 ft. 6 in. for the lower 13 ft. 6 in., and 9 ft. for the remainder. For 13 ft. 6 in. high the tower wall is built up of six rings; for the next 10 ft., of five rings, followed by 11 ft. 8 in. of four rings, and for the remainder of the height of only three rings. At each point at which the tower walls are reduced in thickness, special bonder courses are inserted. The tower is built with an inclined floor, which discharges into a mud-catcher, and is provided with an opening, 15 in. by 2 ft. 2 in. wide just above the top of the mud-catcher, to facilitate cleaning. When the tower is working the opening is closed with a movable acid-resisting block. The mud-catcher is a cylindrical box, 4 ft. 6 in. diameter and 4 ft. 6 in. deep, built up of acid-proof bricks inside a leaden dish of 30-lb. lead. The tower top is built up of acid-resisting blocks in the form of a dome, 7 ft. 5 in. radius, and is pierced with a 24-in. diameter gas outlet, and five to nine spray blocks for the atomisers or sprays.

Tower Off-Takes.—In the earliest plants the gas from the top of the tower passed into the bottom of the recuperator and out at the top, but the concurrent system shown on Fig. 104 has been installed on later plants, as it was found to give better results, owing to the decreased resistance offered to the passage of the gas. The 24-in. off-take is formed of silicon iron pipes, and is taken centrally from the top of the main tower and led at a slight slope into the top of the

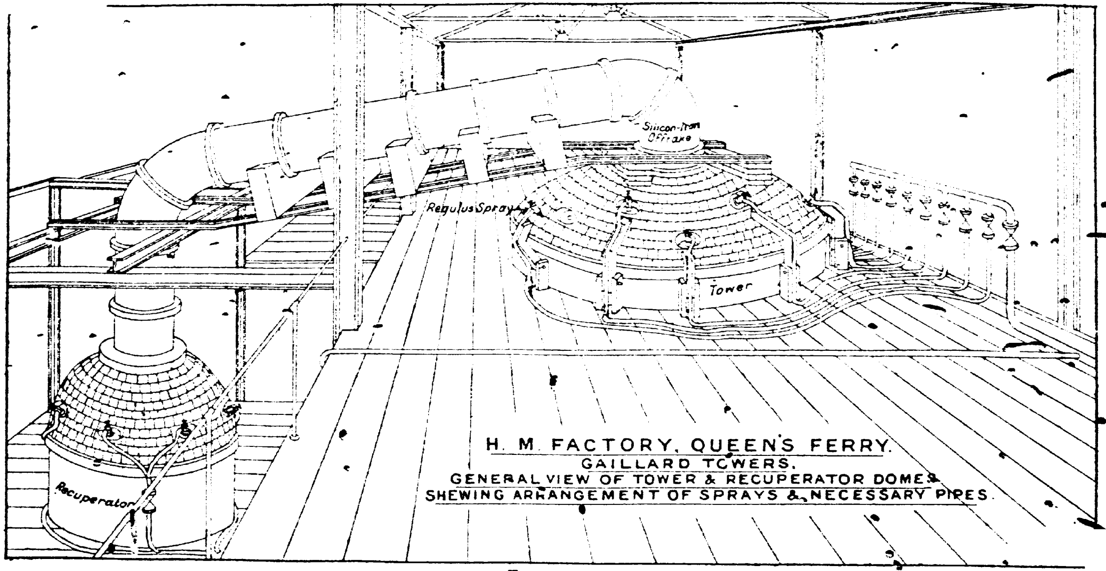
H. M. FACTORY, QUEEN'S FERRY.
GAILLARD TOWERS.
GENERAL VIEW OF TOWER & RECUPERATOR DOMES
SHEWING ARRANGEMENT OF SPRAYS & NECESSARY PIPES.
Silicon-Iron Offtake
Regulus Spray
Tower
Recuperator

FIG. 104.

recuperator tower, which is built with acid-resisting bricks in the shape of a dome to receive it.

Recuperator.—The recuperator consists of a lead-covered tower, 30 ft. 8 in. high and 5 ft. external diameter, built up of acid-resisting blocks two rings thick for the first 14 ft. 4 in., and one ring for the remainder. The diameter of the lower portion is 4 ft., and of the upper, 4 ft. 5½ in. The blocks are erected on top of an acid-proof base inside a leaden saucer, and the bottom course is built so as to allow the acid to overflow at a height of 2½ in. above the base of the tower.

Scrubber.—From the base of the recuperator the gases pass through 24-in. lead-covered earthenware pipes to the bottom of the scrubber, which consists of a lead-lined wooden box 30 ft. by 16 ft. by 11 ft. deep, packed with graded coke. The bottom of the scrubber is covered with acid-proof tiles, on which a brick chequer work is built to facilitate the even distribution of the gas, and to provide a support for the coke packing. The sides of the scrubber are protected by an acid-proof lining tile 1½ in. thick, up to a height of about 6 ft. When the spaces in the brick grid chequer work are filled with large pieces of coke, the whole surface is covered with an 8-in. layer of coke, 4 in. in size, and then with a 4-in. layer of coke, 1½ in. to 2 in. in size. The remainder of the scrubber is packed with coke graded regularly from 1½ in. to ⅜ in. The gas passes from the top of the scrubber through an 18-in. lead pipe to the fan placed underneath the scrubber.

Fan.—The draught through the system is produced by a high-pressure Kestner fan, two sizes of which are in use: (1) 16 in.; (2) 21 in. (two designs).

The fans are belt-driven, and the gases are exhausted through an 18-in. main into the flues of the Cottrell precipitator.

Acid Circulation.—From the feed acid storage tanks the weak acid gravitates to eight lead-lined horizontal cast-iron eggs, each 4 ft. 2 in. internal diameter, and 18 ft. 6 in. long, built up in three sections, with two spherical ends fitted with manhole covers. Each pair of towers is supplied by two eggs, which are connected with the atomisers at the top of the towers and recuperators by means of 1½-in. lead main, through which the acid is blown by compressed air at a pressure of 80 lb. per square inch. The concentrated acid from the base

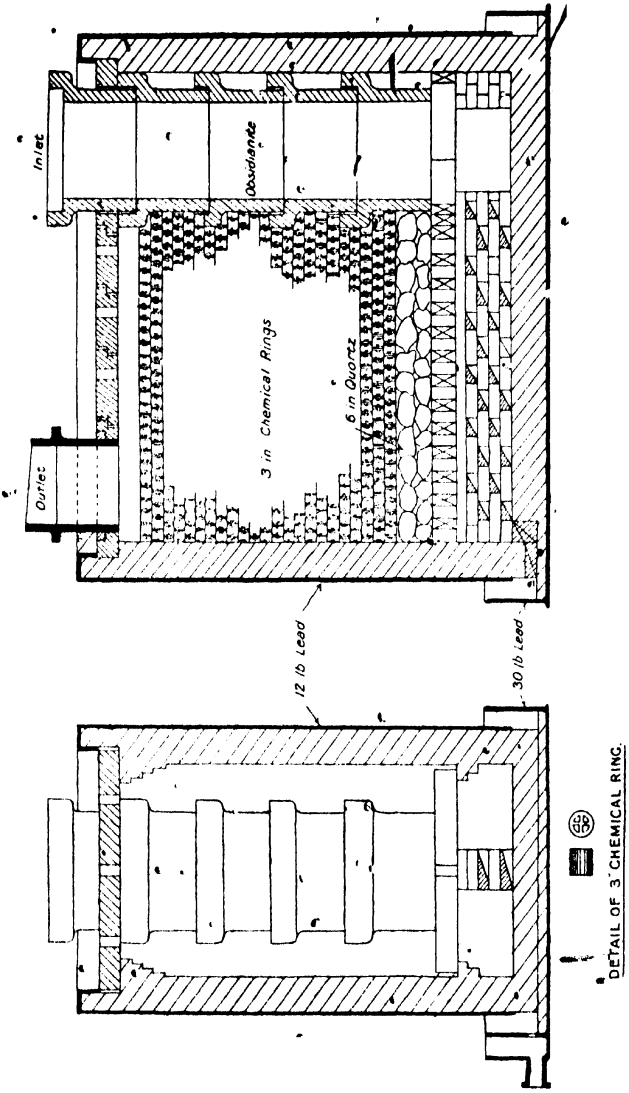
Inlet
Outlet
Obsidianite
3 in Chemical Rings
6 in Quartz
12 lb Lead
30 lb Lead
DETAIL OF 3" CHEMICAL RING.

FIG. 105.

of the tower flows through the mud-catcher into a cooler, 3 ft. 6 in. internal diameter by 4 ft. 8 in. deep, fitted with an external water-jacket and three lead cooling coils. From the coolers the concentrated acid flows away to storage tanks.

The Counter-current System of working the Recuperator compared with the Concurrent System.—With a 16-in. Kestner fan running at 1440 r.p.m., the average draught on the two systems was as follows:—

	Counter-current. Inches of Water.	Concurrent. Inches of Water.
Furnace	0·2	0·1
Tower outlet	0·5	0·6
Recuperator outlet	2·0	0·9
Fan	3·7	2·4

The output was increased from 40 to 45 tons per twenty-four hours of 92 per cent. H_2SO_4 from a feed acid of 65 to 66 per cent. to 60 tons per twenty-four hours, by the alteration to the concurrent method of working the plant.

Recent Improvements.—In the latest installation further improvements have been made by (*a*) the substitution of a "box" type of recuperator; (*b*) the substitution of pumps for elevating the acid in place of eggs; (*c*) the installation of a cooler for the acid leaving the base of the recuperator tower.

(a) "*Box*" *Recuperator.*—This consists of a 12-lb. lead box, 11 ft. 3 in. by 6 ft. by 10 ft. 9 in. high, standing in a 30-lb. lead saucer, and lined with 9 in. of acid-resisting brickwork. The 24-in. inlet pipe is built of obsidianite inside the recuperator, and the outlet from the top consists of a 21-in. lead pipe. The gas passes from the base of the obsidianite inlet pipe through chequer brickwork, and a 6-in. grid of acid-proof slabs, spaced 3 in. apart, and then through two layers of 6-in. quartz. On top of this are placed two 3-in. layers of chequer brickwork, and then the main packing of the recuperator, which consists of 3-in. pottery rings of the standard pattern The rings are followed by several courses of 3-in. brick chequer, and the recuperator is covered by brick slabs 5 ft. 1 in. long. The cover is fitted with a series of lutes, to ensure an even distribution of acid.

(b) *Acid Circulation.*—The weak acid from the feed acid storage tanks gravitates to a set of three cast-iron centrifugal pumps, and is elevated to a constant head storage tank, from which it flows to a series of small lead-lined tanks, immediately over

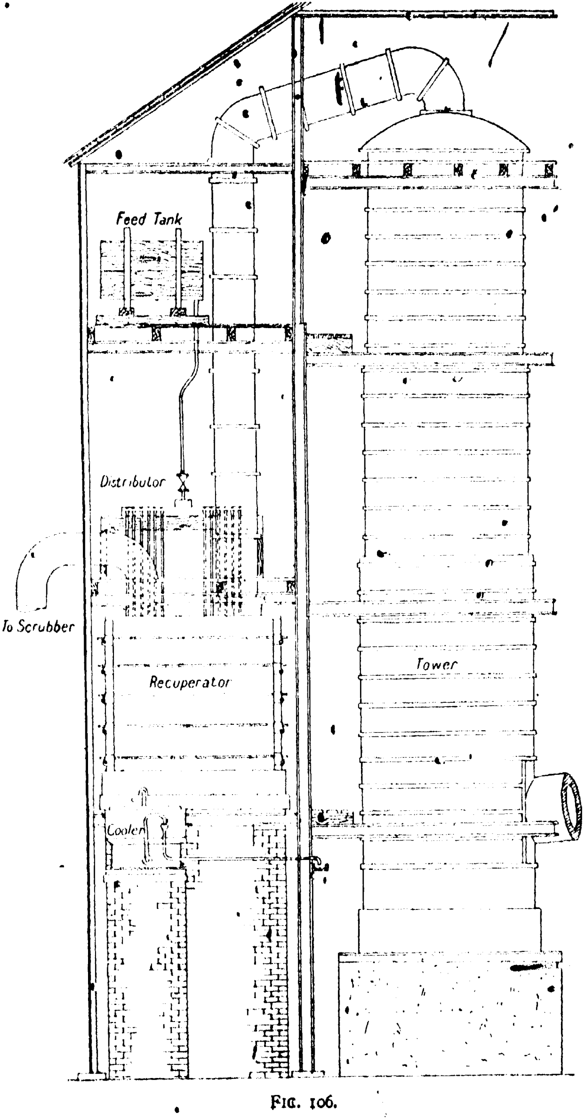
Feed Tank
Distributor
To Scrubber
Recuperator
Cooler
Tower

FIG. 106.

the tops of the box recuperators, and is fed into the distributors and lutes. The acid which collects at the base of the recuperators passes through a cooler and then flows to storage tanks for the main tower on the ground level. All the weak acid to be concentrated thus passes through the recuperator before being fed to the main tower. From the ground level storage tanks the acid is elevated by three centrifugal pumps to two lead-lined storage tanks on an extension of the tower top platform. A further three pumps are installed to deliver the acid from these tanks to the atomisers.

The Gaillard Plant at Gretna.

The author is indebted to the courtesy of Mr J. C. Burnham, Superintendent, H.M. Factory, Gretna, for permission to abstract the following particulars of the Gaillard plants from his Report H.M. Factory, Gretna, "Description of Plant and Processes" (pp. 101-108).

Gas Heating System.—The producer gas is conveyed from a central producer plant through a 36-in. brick flue, and to each furnace through two 8-in. screw gas valves. The gas is burned in a combustion chamber (9 ft. long—internal—by 9 ft. wide) by the admission of air through two 9-in. primary air ports, in front of the furnace. Secondary air is admitted through 6-in. secondary air ports, and the whole of the gases are then passed through a brick chequer into a brick-lined steel chamber.

Main Tower.—The hot gases from the chamber pass through a 23½-in. diameter pipe into the base of the main tower, which is 50 ft. in height and 10 ft. 8 in. internal diameter. The tower is built of volvic stone of an average of 8 in. thickness, the actual thickness decreasing from bottom to top, and is lead-covered and supported by iron bands spaced about 18 in. apart. The tower is erected inside a saucer of 30-lb. lead, and the volvic stone floor slopes towards the acid outlet (25 in. by 14 in.), which discharges into a cylindrical sludge box (5 ft. internal diameter by 5 ft. deep) built of acid-proof tiles, and lead-covered. A special removable sludging stone is provided, to facilitate the cleaning of the tower base. The acid flows from the sludge box through a 6-in. Narki metal bend into a cooler similar to that described on p. 208, and flows then to the concentrated acid storage tanks.

Recuperator.—The gases leave the top of the tower through a 22-in. diameter outlet, and pass through lead-covered earthenware pipes to the recuperator, which consists of a stone chamber, 6 ft. 6 in. by 4 ft. 11 in. internal dimensions, covered with lead, and standing in a lead saucer. The chamber is packed with acid-proof bricks over which a regular flow of acid is maintained to cool the hot gases.

Scrubber.—The scrubber is a leaden box (31 ft. by 15 ft. by 12 ft. high) of the usual type, and the packing consists of about 8 in. of 4-in. coke, 8 in. of 2 to 2½-in. coke, and 7 ft. 6-in. of coke graded from 1½ to ⅜ in. The gases pass upwards through the packing, and leave the scrubber top through an 18-in. outlet pipe leading to the 16-in. Kestner fan, which produces the draught through the system. The fan runs at a speed of 1800 r.p.m., and moves approximately 3600 cub. ft. of gas at a temperature of 80° C., with a suction at the fan inlet of 6½-in. water-gauge. The exit from the fan is connected with a 19-in. lead pipe, through which the fumes are discharged into the atmosphere above the roof of the building.

Acid Circulation.—The feed acid gravitates from the storage tanks to the lead-lined cast-iron eggs, each of which holds approximately 8½ tons of the usual feed acid (70 to 75 per cent. H_2SO_4). The acid is elevated through a 1½-in. lead pipe by means of compressed air at 90-lb. pressure, to a spray main common to all the towers. Each tower is fed by five 1-in. branches connected to an atomiser or spray. The sprays are classified according to the diameter of the orifice in tenths of millimetres, the two largest sizes being "50's" and "60's," which correspond to orifices of 5 mm. and 6 mm. respectively. The feed capacity of a "60" spray at 40-lb. pressure, equals 1 ton per hour. The acid for the recuperator is pumped from the weak acid storage tanks to the feed tanks above the distributors and fed in through the lutes. The hot acid from the base is run through coolers and then into storage tanks, from which it can be drawn either to the feed eggs or to the pumps.

Output.—The plant is capable of producing 90 tons of 92 per cent. C.O.V. per tower per day from a feed acid of 70 to 78 per cent. acid with a 99 per cent. recovery.

The following figures on the concentration of sulphuric acid by the Gaillard tower are abstracted from the Report of the Statistical Work of the Factories Branch of the Department of Explosives Supply, Ministry of Munitions (pp. 143 and 144):—

H.M. Factory, Queen's Ferry.
Monthly Report.

Month ending 6 A.M., 29th December 1917.

GAILLARD TOWERS RECORD.

Sulphuric Acid Concentrators (T.N.T.).

Units Working, 11·2.

Charged.	Tons.	Per cent. H_2SO_4.	Tons H_2SO_4.	Tons SO_3.	Produced.	Tons.	Per cent. H_2SO_4	Tons H_2SO_4.	Tons SO_3.
Sulphuric acid	15313·6	66·10	10122·4	8262·7	Sulphuric acid	10968·5	90·01	9873·7	8060·0
Fuel— Coal used .	1449·1	...	...	...	...	...	..	...	...

Lost.

Sulphuric acid—	Tons.	Tons SO_3.
Total H_2SO_4 charged to plant . .	10122·4	8262·7
Total H_2SO_4 recovered . . .	9873·7	8060·0
Amount lost	248·7	202·7

Per cent. lost, 2·45 per cent.

Stocks.

	Tons.	Per cent. H_2SO_4.	Tons H_2SO_4.	Tons SO_3.
Stock denitrated acid on 1st December . .	706·0	66·4	468·8	382·7
Stock weak sulphuric acid	...	...	97·6	79·9
Denitrated sulphuric acid received . .	15635·9	66·00	10320·2	8424·0
Weak sulphuric acid received, Grillo . .	31·8	61·63	19·6	16·0
" " " cascades .	303·4	88·76	269·3	219·9
Total	...	...	11175·5	9122·5
Concentrated acid issued to mixing plant .	11172·4	90·02	10057·7	8210·2
Sulphuric acid issued to cascades	412·4	66·46	274·1	223·8
Stock of denitrated sulphuric acid on 29th December	715·0	66·0	471·9	385·2
Stock of weak sulphuric acid . . .	...	...	123·1	100·6
Lost in concentration	...	...	248·7	202·7
Total	...	...	11175·5	9122·5

Physical Data, etc.

Gases.	Pressure. Inch (water).	Temperature. °C.	CO.	CO$_2$.	Grams H_2SO_4 per 100 Litres.
Leaving producers	...				
Entering furnaces	0·8	300 to 350			
,, tower	0·3	900 ,, 1050			
Leaving ,,	–0·5	205 ,, 235			
Entering recuperateur	–1·0	200 ,, 220			
Leaving ,,	–2·0	130 ,, 150			
Entering scrubber	–2·5	120 ,, 140			
Leaving ,,	–4·0	90 ,, 100			
Entering Cottrell precipitator	0·1	80 ,, 90			
Leaving Cottrell precipitator	–0·8	75 ,, 77			

Acids.	Per Cent. H_2SO_4.	Temperature. °C.	Tons.
Charged to towers	66·10	24 to 26	15313·6
Leaving towers	90·01	22 ,, 23	10968·5

Electrical Data.	Amps.	Volts.	K.W. Hours.
Current supplied to Cottrell precipitator	1041	329 to 424	...
Power consumed	...	...	10537
Voltage at precipitator	...	65237	...
Power consumed by fan	...	...	3988·3

General.	
Tons concentrated per tower (H_2SO_4, 90·01 per cent.)	46·6
Total acidity of exit gases (at precipitator)	...
Coal used per ton of concentrated acid (H_2SO_4, 90·01 per cent.)	0·132
,, ,, H_2SO_4 produced	0·147
,, ,, water evaporated	0·353
Water evaporated per tower per 24 hours	13·7 tons

The following figures on the efficiencies of Gaillard towers are abstracted from the "Second Report on Costs and Efficiencies for H.M. Factories," issued by the Department of Explosives Supply, Ministry of Munitions:—

January-June 1918.

Factory.	Production. Tons H_2SO_4.	Loss.	Efficiency.
Gretna	31280·2	1·3	98·7
Oldbury	26847·0	7·7	92·3
Queen's Ferry	68798·9	2·0	98·0
Average	126926·1	3·1	96·9

The Operation of a Gaillard Tower.

General Principles.—The Gaillard system of concentration consists essentially of the spraying of weak acid down an empty tower up which a current of hot gas is ascending. Under these conditions, contact between the acid and the hot gas is as intimate as possible, and the evaporation of the liquid takes place at a temperature considerably below the boiling-point of the sulphuric acid.

Heating System.—The heat required for concentration is obtained by the combustion of gas from a producer plant. For small installations a coke-producer of the intermittent type, similar to that frequently employed with the Kessler plant, is very common, but for regularity of output and strength of acid, either a continuous producer or a twin furnace similar to that described on p. 171 is preferable. For very large installations, it is usual to erect a central gas-producing plant, which supplies a battery of towers with gas that is burned in specially designed furnaces at the base of each tower.

The two main factors which govern the output and strength of the concentrated acid are: (1) a regular supply of heat at a uniform temperature; (2) a regular supply of acid at a constant strength. The first factor is much more difficult to control than the second, so that, given a constant fan draught, a careful regulation of the temperature of the furnace gases is the first essential to successful working. For this purpose it is a great advantage to indicate the temperature in the exit-flue from the furnace by means of a recording pyrometer, and, with large installations, to house the continuous recorders in a central position on the plant, so that the working conditions on each unit can be observed readily. With gas-fired furnaces, the temperature of the hot gases entering the main tower is controlled and regulated by the quantity of gas burned, so that adjustments (when necessary) can be carried out promptly and accurately.

With a continuous or non-continuous producer, the regulation of the temperature is governed chiefly by the volume of secondary air admitted. To secure the optimum results in working the producer, it is essential to restrict the supply of air passing through the combustion chamber, so that a large proportion of carbon monoxide is formed, and is carried forward and burned to carbon dioxide by the admission of an excess of secondary air in the mixing chamber of the furnace immediately in front of the entrance to the main tower. The secondary air passing through a series of flues built in the walls of the furnace is raised in temperature by the heat radiated from the walls, and, by this means, the lining of the combustion chamber is cooled. The reduction in temperature tends to preserve the brickwork and to lengthen the life of the furnace. At regular intervals, as a guide to the working of the plant, the percentage of carbon dioxide in the gases entering the main tower is tested by means of the Orsat apparatus. To secure the best results, the volume of secondary air is adjusted to give a carbon dioxide content of 7 to 9 per cent. in the gases. A lower test indicates an excess of air, which tends to reduce the inlet temperature, and so lower the capacity of the plant; while a higher test corresponds with high inlet temperatures, which tend to dissociate the sulphuric acid into sulphur trioxide and water. From experience it has been found that the best conditions for steady and economical work are obtained when the inlet temperature is maintained at approximately 1000°.

The life of the furnace depends on its treatment. Sudden fluctuations of temperature cause undue expansion and contraction of the firebrick lining, and quickly bring about a rapid deterioration and collapse. When lighting up a plant, therefore, a small fire is maintained for several days to dry the brickwork thoroughly before raising the temperature gradually to the normal working level. Once this has been reached, it should be maintained as closely as possible.

Main Tower.—The main tower acts merely as a flue or hollow shaft, through which the hot gases and acid spray pass in opposite directions, and its life depends, therefore, on the acid-resisting qualities of the material of which it is constructed. The principal material used for this purpose is volvic stone, which resists both acid and heat with remarkable success. It is found at Volvic (Puy-de-Dome), in the centre of France, and can be obtained in large blocks, which are shaped easily to any required design.

Within the last decade, towers have been built of other types of acid-resisting material which have given good satisfaction. Typical examples of these "artificial" acid-resisting stones are: (1) obsidianite; (2) "Nori" ware.

The first-named material is manufactured by Messrs Charles Davison, Ewloe Barn, near Chester (see p. 115), in the form of curved blocks, and a description of a tower of this type has been given above (p. 200).[1] The second-named material is manufactured by the Accrington Brick & Tile Co., Ltd., Accrington, in the form of 3-in. bricks, and a description of a tower of this type has been given above (see p. 211).

The hot gases enter the main tower at 900 to 1000°, and are reduced in temperature by contact with the acid spray falling down the tower, so that they leave the top at a temperature of 200 to 220° C. This exit temperature is the chief guide to the working of the plant, and is indicated by means of a recording pyrometer, so that any variation in temperature can be observed promptly and its cause investigated. If the temperature rises there are two courses to adopt: (1) increase the flow of acid down the tower by bringing into use larger or additional atomisers; (2) increase the volume of secondary air to the furnace. Very sudden rises in temperature may be due to: (1) choking of the atomisers or defective spraying; (2) loss of air pressure; (3) feed egg blown dry.

Given a constant flow of hot gas at a uniform temperature into the base of the tower, the concentration of the acid falling down to the bottom of the tower is governed by the volume of acid and its degree of fineness of atomisation. The quantity of acid fed into the tower is varied by altering the number of atomisers in use, and the greater the degree of fineness of atomisation, the greater is the surface exposed to the evaporative action of the hot gases, and hence the greater the degree of concentration effected. By varying the number and size of the atomisers working on the tower, the volume of acid passing down can be adjusted at will. It is never altered by throttling down the valve on the spray pipe, as it is impossible to know accurately what has been the amount of throttling thus effected. The greater the pressure of the air on the atomiser, the greater is the volume of acid passed, and the finer the degree of atomisation. With a standard pressure of 90 lb. per square inch on the acid eggs at the foot of the tower, there is a loss of approximately 50 lb. caused by the lifting of the acid to the top of the tower, so that the ordinary spraying pressure is approximately 40 lb. per square inch. At this pressure a spray with an opening of 6 mm. diameter (a No. "60" spray) will pass 1 ton of acid per hour. The sprays are fitted into specially prepared openings, placed symmetrically in the tower top. The number of these holes provided varies with the size of the plant, but from five to nine is the usual number.

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[1] See also *J. Soc. Chem. Ind. (Trans.)*, 1921, pp. 257-265.

In plants where the tower is constructed of volvic stone, the top is usually flat and built up of volvic slabs, jointed together; but in recent installations where the tower is erected entirely of acid-resisting brick, the top is built up in the form of a dome, and provided with a central opening for the gas outlet. It is advisable to maintain a slight suction on the dome, as a positive gas pressure at this point leads to a rapid deterioration of the dome, due to the leakage of gas and sweating of the acid through the joints. Hence it is necessary to provide an off-take from the tower top, to conduct them away to the recuperator, of sufficient capacity to prevent any throttling of the gases. The off-take is formed either of lead-covered earthenware pipes or of acid-resisting silicon iron pipes. It is a decided advantage also to slope it in such a way that any condensed acid will drain away into the vertical section, instead of lying in the joints or cracks, and finally making its way through them (Figs. 104 to 107).

Recuperator.—The gases from the top of the main tower entering the recuperator at a temperature of 200 to 210° C., carry over a certain quantity of acid mist with them, which

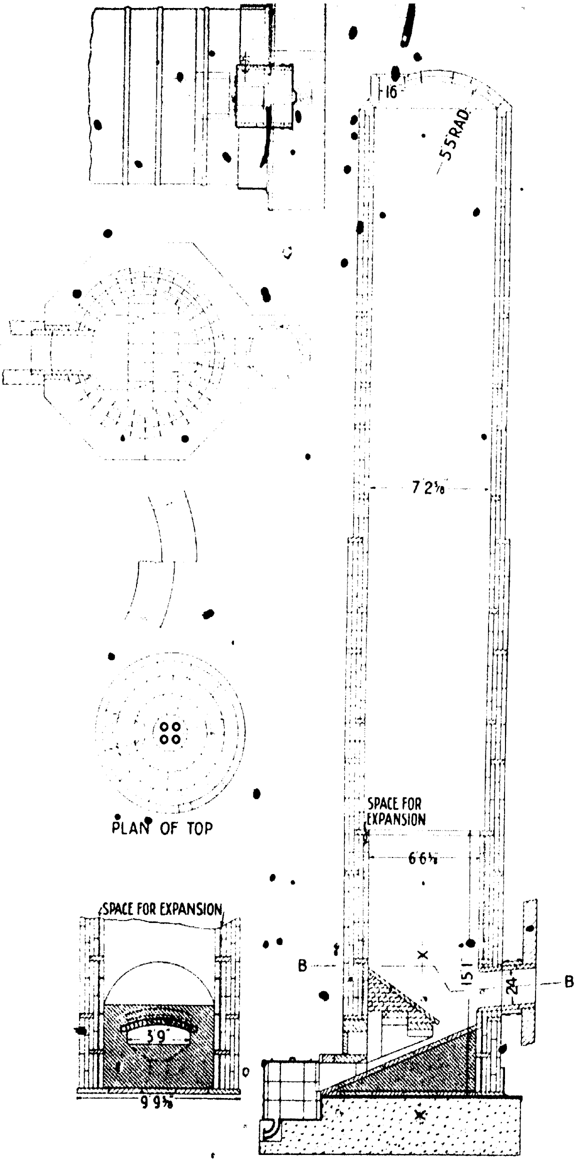

FIG. 107.—Gaillard Tower in Obsidianite Blocks.

is trapped in the recuperator, and amounts to approximately 7 to 8 per cent. of the output of the plant. Three types of recuperators are in general use: (1) the original tower form, in which the gases enter at the bottom and rise counter-current to the stream of atomised acid; (2) the concurrent tower type, in which the acid and gas flow in the same direction down the tower; (3) the box type, in which the gases pass through a chequer work of acid-resisting bricks over which a large volume of acid is circulated. The object of the three types is identical—viz., to cool the gases down, so that they can be passed safely to a coke scrubber, and to trap acid mist. The flow of acid down the recuperator is regulated so that the gases leave the tower at a temperature above their saturation point for water vapour.

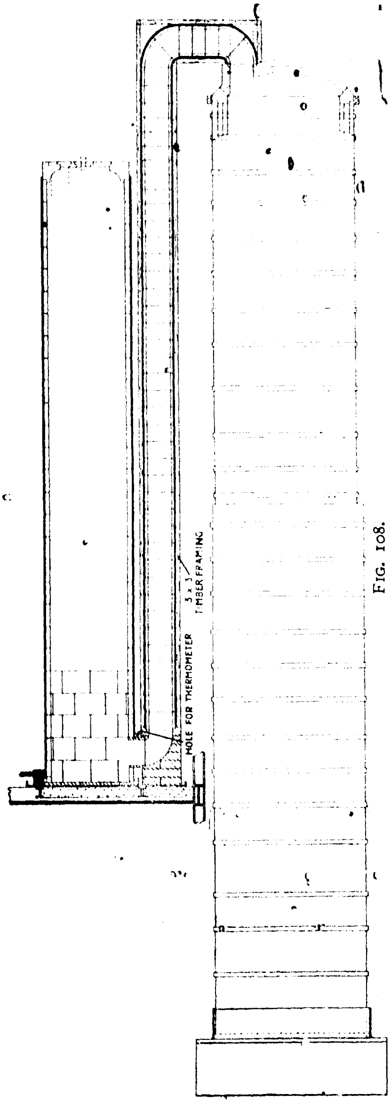

Fig. 108.

With the original counter-current type of recuperator tower, Figs. 108 and 109, the temperature of the exit gases varies from 110 to 120°, while the acid leaves the base at a temperature of 150 to 160°. With the concurrent recuperator, the gases leave at a temperature of 135 to 150°, according to the volume of acid sprayed down the tower, while the acid overflows from the base at a temperature of about 125°. With the box type of recuperator, the flow of acid is regulated so that the gases leave at about 140°. There is a slight concentration effected in the recuperator, due mainly to the acid mist pulled over mechanically from the main tower. The necessity for maintaining a slight suction on the top of the main tower has been pointed out above, but an excessive pull is also uneconomical for the following reasons. Any acid fed into the main tower, but drawn over into the recuperator, is lost to the strong acid, and recovered only in the weak acid system, so that the work of lifting it to the top of the tower, and the wear and tear involved, are so much dead loss. Furthermore, the mist is not drawn over at the strength of the feed acid entering, but at a strength appreciably higher, so that the heat used in concentrating this acid is also lost, as the mist absorbs water vapour in the recuperator tower, and is diluted down again. Hence, the quantity of mist drawn over should be reduced to a minimum consistent with the maintenance of satisfactory working conditions on the main tower.

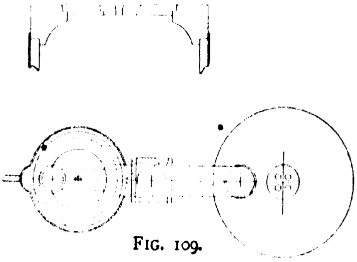
FIG. 109.

From actual experience[1] it has been found to be most economical to use the weakest acid to be concentrated on the recuperators. The weaker acid not only traps more acid, and cools the gases better than the same volume of stronger acid, but it also brings down less water from the gases. For this reason all the weak acid from the scrubbers and fan drips, etc., is put through the recuperator before being sprayed into the tower.

Scrubber.—The scrubbing of the gas from the recuperator, laden with acid mist, serves two distinct purposes: (1) to improve the efficiency of the plant by preventing loss into the atmosphere of the maximum amount of weak acid, which can be returned economically to the concentrators for use again; (2) to render the gas passing into the exit pipe to the atmosphere as innocuous as possible. The gas, leaving the recuperator at a temperature just above its saturation point for water vapour, is cooled still further in the scrubber by (1) radiation of heat; (2) by the circulation of weak acid over the coke packing; and (3) by water-cooling the leaden top of the scrubber. Condensation takes place rapidly in the finely divided coke packing, and the weak acid thus formed falls to the bottom of the scrubber, and is run away to storage tanks. The strength of the precipitated acid varies directly with the temperature at which condensation takes place. As the temperature falls, the strength of the acid decreases, but the quantity of weak acid increases. With an unlimited cooling capacity, the process can be continued until the whole of the water evaporated in the concentrators has been recovered in the form of weak acid, of ever-diminishing strength. In practice, the capacity of the scrubber is fixed, so that it yields an acid of not less than 50 to 60 per cent. H_2SO_4, which is utilisable again on the plant. In some works the scrubber acid is cooled and circulated over the coke packing, to improve the efficiency of condensation, and at the same time to increase the percentage strength of the acid (see p. 205).

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[1] J. C. Burnham, H.M. Factory, Gretna, p. 106.

Fan.—The type of fan most frequently employed for drawing the hot gases through the plant is the high-pressure fan supplied by Messrs Kestner of London. Prior to 1915, the standard size was a 12-in. high-pressure fan, but, with the rapid development in the capacity of the Gaillard unit during the period 1915-1918, much larger fans came into use. The most generally adopted size is the 16-in. fan, running at 1000 to 1800 r.p.m., and capable of dealing with approximately 2000 cub. ft. per minute. The actual volume of gas passing will depend upon the resistance of the various sections of the plant.

For large diameter towers, concentrating up to 100 tons per twenty-four hours of 93 per cent. sulphuric acid, a 21-in. high-pressure fan, running at 1500 r.p.m., is employed, which is designed to handle 6000 cub. ft. of gas at 100°, with a water-gauge of 7 to 8 in. at the fan. The shaft carrying the impeller runs in bronze bearings, lubricated with oil. The oil-bath is cooled by means of a small copper coil immersed in it, through which water is circulated. The fans may be direct-coupled to an electric motor; in which case a variable speed control is required, or may be belt-driven, and the speed regulated by adjusting the size of the driving pulley on the motor.

Owing to the high speed at which the fans run, it is essential that the impeller should be carefully balanced before use, and replaced as soon as it shows signs of loss of balance. The most frequent cause of breakdown is due to the regulus metal becoming detached from the phosphor bronze blades, and hence it is advisable to maintain as regular a temperature as possible in the fan casing, so that the wear and tear is reduced to a minimum. For the same reason, the temperature of the gases passing through the fan should not exceed 80 to 100°.

A further condensation of acid mist is produced by the action of the fan blades, and the weak acid runs from the base through a lute to a collecting tank. The gas is delivered from the fan into an exhaust duct, which is carried up above the roof of the main tower building, and is discharged into the atmosphere. A small quantity of weak acid is condensed in the exhaust pipe and runs back to a collecting tank.

Exit Gases.—The exit gases consist chiefly of steam, with a slight trace of acid mist, the acidity of which depends upon the efficiency of the scrubber, but should not exceed two grains SO_3 per cubic foot. The acid mist leaving the exit is very difficult to condense, as it exists in a form which is not effected by mere cooling, and hence it is usually referred to as "vesicular" fume, *i.e.*, it is assumed that each droplet of acid acts like a hollow ball and rebounds from any surface with which it comes in contact. According to a more recent theory,[1] the explanation for the behaviour of these fumes is to be found in the repulsive action of the electrical charges on the droplets. When exposed to surface friction or to the action of the high-tension electric current, the droplets or spheroids are de-electrified by reason of the neutralisation of their charges, and lose their individuality and coalesce together. The exit gases are sampled continuously by means of an aspirator, and analysed regularly to check the loss of acid by escape from the plant. As a guide to the working of the plant, "bellows" spot tests are made every few hours by means of a Fletcher aspirator. The gases are shaken with a weak solution of hydrogen peroxide, and the acidity estimated as SO_3 by titration with standard caustic soda solution. The presence of SO_2 in the exit gases is estimated by means of the Reich test, and indicates that dissociation of H_2SO_4 into SO_3 and H_2O, and then into SO_2, is taking place in the main tower, due to excessive local heating.

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[1] *Technical Records,* Ministry of Munitions, No. 3, p. 52.

Control of the Working of a Gaillard Tower.

As a guide to the working of the plant, the strength of the acid leaving the cooler is determined every half hour. As the acid frequently contains impurities (such as iron sulphate, lead sulphate, etc.) which raise the specific gravity recorded by the hydrometer, it is often advantageous to adopt the heat rise method. The method is based on the rise of temperature produced when sulphuric acid is diluted with water, and is described by Howard.[1]

The following is the method as adopted by Messrs Kynoch, Ltd., since 1911-1912.

Into a porcelain cup of 500 c.c. capacity, 100 c.c. of cold water are measured and the temperature recorded. The sample of acid to be tested is cooled down to the temperature of the water, 12 c.c. are run out from a small burette into the water, and the mixture well stirred with a thermometer. The rise of temperature is recorded, and from this figure the strength of acid is obtained by means of the appended table. (The figures vary slightly with the apparatus, which is calibrated before use.)

[1] *J. Soc. Chem. Ind.*, 1910, pp. 3-4.

Percentage of H_2SO_4 in Sulphuric Acid and Oleum for a Given Heat Rise.

Centigrade Heat Rise.	Percentage H_2SO_4.	Centigrade Heat Rise.	Percentage H_2SO_4.	Centigrade Heat Rise.	Percentage H_2SO_4.
25·0	93·2	31·0	99·0	36·5	102·5
25·5	93·6	31·5	99·5	37·0	102·7
26·0	94·1	32·0	99·9	37·5	103·0
26·5	94·6	32[illegible]	100·3	38·0	103·2
27·0	95·1	33·0	100·6	38·5	103·5
27·5	95·6	33·5	100·9	39·0	103·8
28·0	96·1	34·0	101·2	39·5	104·1
28·5	96·5	34·5	101·5	40·0	104·4
29·0	97·0	35·0	101·7	40·5	104·7
29·5	97·5	35·5	102·0	41·0	105·0
30·0	98·0	36·0	102·2	41·5	105·3
30·5	98·5	...	...	...	...

A slightly longer, but more accurate, method is described by Curtis and Miles.[1] In every case the samples should be cooled to 25° or lower.

A. *Test for Oleum* (of not more than 25 per cent.).—200 c.c. of oleum (temperature a° C.) are poured quickly, with vigorous stirring, into 200 c.c. of sulphuric acid (92·5 to 94·5) at b° in a straight sided earthenware mug holding about a pint. The rise of temperature $= C - \frac{1}{2}(a + b)$ where C is the maximum temperature of the mixture. The percentage of free SO_3 is found from Table 1. After mixing, the liquid should not fume. The results are reliable within 0·5 per cent. free SO_3 or 0·1 per cent. H_2SO_4.

B. *Test for Sulphuric Acid* (96 to 100 per cent.).—The procedure is as above, but the acid is poured into the oleum (20 to 25 per cent.). Rise $= C - \frac{1}{2}(a + b)$ as before. Table 2 is used for this purpose. After mixing, the liquid should fume. The results are reliable within 0·3 per cent. H_2SO_4.

C. *Test for Sulphuric Acid* (88 to 96 per cent.).—100 c.c. of the acid sample (temperature b°) are mixed with 300 c.c. of oleum (20 to 25 per cent. temperature $= a^\circ$). Rise $= C - \frac{1}{4}(3a + b)$. Table 3 is used here. After mixing, the liquid should fume. The error should be less than 0·5 per cent. H_2SO_4.

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1920, p. 64.

Table 1.				Table 2.		Table 3.			
Rise.	Per cent. SO_3.	Rise.	Per cent. SO_3.	Rise.	Per cent. H_2SO_4.	Rise.	Per cent. H_2SO_4.	Rise.	Per cent. H_2SO_4.
1	0·5	21	12·1	...	...	6	98·8	26	92·6
2	1·1	22	12·8	...	...	7	98·5	27	92·3
3	1·6	23	13·4	2	99·9	8	98·1	28	92·1
4	2·2	24	14·1	4	99·5	9	97·7	29	91·8
5	2·7	25	14·7	6	99·3	10	97·4	30	91·6
6	3·3	26	15·4	8	99·9	11	97·1	31	91·3
7	3·8	27	16·0	10	98·7	12	96·7	32	91·0
8	4·4	28	16·7	12	98·4	13	96·4	33	90·8
9	4·9	29	17·4	14	98·1	14	96·1	34	90·6
10	5·5	30	18·0	16	97·8	15	95·7	35	90·3
11	6·1	31	18·7	18	97·5	16	95·5	36	90·1
12	6·7	32	19·4	20	97·3	17	95·1	37	89·8
13	7·3	33	20·1	22	96·9	18	94·9	38	89·6
14	7·9	34	20·8	24	96·2	19	94·6	39	89·4
15	8·5	35	21·5	26	96·4	20	94·3	40	89·1
16	9·1	36	22·2	28	96·1	21	94·0	41	88·9
17	9·7	37	22·9	30	95·8	22	93·7	42	88·7
18	10·3	38	23·6	...	...	23	93·4	43	88·5
19	10·9	39	24·3	...	...	24	93·1	44	88·2
20	11·5	40	25·0	...	...	25	92·9	45	87·9

The Mechanism of Concentration.

Very little data is available of the actual stages in the process of concentration, but a rough outline of the probable course of events may be obtained if the system is considered as one of static equilibrium $\left(\frac{p' \, H_2SO_4 \times q' \, H_2O}{p \, H_2SO_4 \times q \, H_2O}\right) = K$ a constant, so that, for any given temperature, a definite equilibrium exists between the concentration of the liquid acid and its vapour.[1]

The finer the degree of atomisation of the weak acid in the top of the tower, the more rapidly is it raised in temperature by contact with the current of hot gases ascending the tower. The concentration of the liquid acid in equilibrium with its vapour will vary directly with the temperature, so that each drop of acid will increase regularly in strength as it falls towards the bottom of the tower, and the concentration of the vapour given off in its fall will also increase proportionally. In actual practice, however, the process is not quite so simple, but is influenced by the relative speeds and temperatures of the gas and liquid in the tower, and usually a small proportion of the acid is dissociated into sulphuric anhydride and water vapour. The hot gases are cooled in supplying the necessary heat of vaporisation to the vapours evolved, and also by radiation. In the recuperator tower they are still further cooled by the injection of weak sulphuric acid, so that they reach gradually their point of saturation of water vapour, after which concentration ceases and condensation occurs.

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[1] *Kaltenbach Chim. et Ind.*, 1921, 5, 143-149.

Experiments carried out at one of the Government factories[1] have thrown further light of an unexpected nature on the mechanism of the process of concentration. Samples of acid collected from a drip on the off-take from the main tower have been found to test much higher in strength than the feed acid injected into the top of the tower, in spite of its close proximity. With a feed acid of 72 to 76 per cent. H_2SO_4 on the main tower, the strength of the drip varies between 86 and 90 per cent. H_2SO_4, and samples as high as 93 per cent. have been obtained under special conditions. The suggestion put forward to explain these facts is that, when sulphuric acid of about 75 per cent. is *sprayed* into an atmosphere at a temperature of approximately 215° to 220°, it is instantaneously concentrated to the neighbourhood of 90 per cent., in spite of the surrounding atmosphere being charged heavily with water vapour. The concentration of the acid will be maintained so long as the temperature is high enough to overcome the affinity of the acid for the water, but the moment it falls, then the water is reabsorbed and weaker acid results.

Date and Time.	Production from Towers in Tons of H_2SO_4.	Tons H_2SO_4 trapped by		Total.	Percentage on Production of Main Tower.
		Recuperator.	Scrubber.		
24 hours ending—					
29/6/17— 2.15 P.M. .	199·0	10·9	5·6	16·5	8·3
4/7/17—11.0 " .	143·1	8·3	6·4	14·7	10·3
9/7/17— 4.15 " .	149·3	6·7	6·6	13·3	9·9
16/7/17—11.15 " .	180·2	11·0	4·5	15·5	8·6

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[1] *Technical Records of Explosives Supply*, No. 3, pp. 49-54.

Experiments were carried out to determine the quantity of acid mist drawn over from the main tower and trapped by the recuperator, and also by the scrubber, and the results obtained are given in the table on preceding page.

At the same time the amount of water charged to the tower and reabsorbed in the recuperator and scrubber was estimated as follows:—

Date and Time.	Sulphuric Acid produced from Towers in Tons of H_2SO_4.	Equivalent Feed at 75 per cent. H_2SO_4.	Weak Sulphuric Acid trapped in Recuperator.	Per cent. H_2SO_4.	Weak Sulphuric Acid trapped in Scrubber.	Per cent. H_2SO_4.	Water expelled from Towers.	Water absorbed in Recuperator and Scrubber.	Percentage of Water re-absorbed.
24 hours ending—		Tons.	Tons.		Tons.		Tons.	Tons.	
29/6/17 — 2.15 P.M. .	199·0	265·3	14·6	74·6	7·9	71·3	50·6	3·5 + 2·3 = 5·8	11·5
4/7/17—11.0 " .	143·1	190·8	11·1	74·6	9·1	71·3	35·8	2·8 + 2·7 = 5·5	15·4
9/7/17— 4.15 " .	149·3	199·1	8·9	74·5	9·3	70·1	36·1	2·2 + 2·7 = 4·9	13·6
16/7/17—11.15 " .	180·2	240·1	14·6	75·1	6·3	71·4	44·4	3·6 + 1·8 = 5·4	12·2

According to the above theory, the gases leaving the main tower contain numberless "spheroids" of relatively strong acid, suspended in an atmosphere of superheated steam, diluted with the furnace gases and excess air. It is believed that each "spheroid" is approximately of the same percentage composition, as the figures show a distinct relationship between the specific gravity of the tower outlet drip and the temperature. These globules of acid absorb water as the temperature falls with the passage of the gases through the recuperator and scrubber, until finally any untrapped globules escape in the air, where a mist consisting of homogeneous spheroids, and not a mixture of an odd few strongly acid among weaker acid spheroids, is obtained.

In the author's opinion the suggestion that feed acid of about 75 per cent. is concentrated instantaneously to approximately 90 per cent. when sprayed into an atmosphere heavily charged with water vapour, is highly improbable, and the data given above can be explained satisfactorily on the basis of the well-authenticated fact that sulphuric acid is dissociated into sulphuric anhydride and water at temperatures such as are found in the lower half of the Gaillard tower (see Vapour Pressure Tables, pp. 24-25).

Re-combination will tend to take place as the temperature falls in the upper half of the tower, but a small percentage is carried forward by the current of gas right through the feed acid and water vapour. This is fully in accordance with the behaviour of sulphuric anhydride mists such as are met with in the purifying processes in the manufacture of oleum, where it is notorious that acid particles can be swept forward not only through drops of weaker acid, but even through water itself. In the case of the Kessler plant there is a steady rise in strength, as the acid falls from plateau to plateau, showing that the concentration takes place regularly in stages down the recuperator tower, and there is no reason to doubt that a similar regular concentration takes place as the acid falls towards the bottom of the Gaillard tower.

Heat Requirements for Concentration.

The following section has been abstracted from *Technical Records of Explosives Supply*, No. 3, pp. 14-20, of the Department of Scientific and Industrial Research.

The fuel consumption on a Gaillard concentrating plant varies not only with the method of working, but also with the concentration range. For most works' practice the following limits will apply:—

(1) Initial feed acid	65 to 78 per cent. H_2SO_4
(2) Final concentrated acid	92 to 96 ,, ,,

The thermal requirements are expressed most conveniently as fuel consumption per ton of product.

The conditions existing in the main tower of the Gaillard plant will be standardised as follows:—

(1) Initial state	Feed acid at 15°
(2) Final state	Concentrated acid at 220°; steam at 220°

A typical example of a Government factory may be taken as:—

(*a*) Initial feed	65 per cent. H_2SO_4
(*b*) Final product	92 ,, ,,

Using the tables compiled by A. W. Porter (see p. 29), the heat required is the sum of two values: (1) heat of total evaporation at constant temperature; (2) sensible heat at constant concentration. Then from Porter's tables (see p. 38) for 1 lb. of SO_3: (1) the sensible heat of acid containing 65 per cent. of H_2SO_4 (*i.e.*, containing 52 per cent. of SO_3) between 15° and 220° = 204 C.H.U.; (2) the heat of evaporation for acid concentrated from 65 per cent. to 92 per cent. H_2SO_4 (*i.e.*, 53 per cent. to 75 per cent. SO_3) at 220° = 352 C.H.U.

$\therefore$ Total heat required = 556 C.H.U.

$\therefore$ For 100 lb. of 92 per cent. H_2SO_4 (75 lb. SO_3) = 75 × 556 = 41,700 C.H.U., or 1 ton = $\frac{41{,}700 \times 2240}{100} = 934{,}100$ C.H.U.

Heat Requirements (using Porter's tables).—The variation of the heat requirements with the strength of the feed acid between the limits 65 to 78 per cent. H_2SO_4 are given below:—

Initial Strength of Acid.	Heat in Calories for a Solution containing 1 gram of SO_3.	Heat in C.H.U. for 1 ton of 92 per cent. H_2SO_4.	Initial Strength of Acid.	Heat in Calories for a Solution containing 1 gram of SO_3.	Heat in C.H.U. for 1 ton of 92 per cent. H_2SO_4.
65	556·0	934,100	72	420·2	706,000
66	536·0	900,500	73	402·0	675,400
67	513·4	862,500	74	385·0	646,800
68	494·0	829,900	75	368·0	618,200
69	474·0	797,000	76	352·0	591,300
70	458·5	770,300	77	337·0	566,200
71	439·0	737,500	78	321·0	539,300

The effect of variation of the final concentration strength (between the limits 92 to 96 per cent.), with a constant initial feed acid (65 per cent.), is given in following table:—

Final Concentration Strength.	Initial Concentration.	Heat in C.H.U. for 1 ton of Product.	Final Concentration Strength.	Initial Concentration.	Heat in C.H.U. for 1 ton of Product.
Per cent.	Per cent.		Per cent.	Per cent.	
92	65	934,100	95	65	1,032,900
93	65	968,200	96	65	1,066,400
94	65	1,000,000	...	...	...

One ton of coal delivers to the Gaillard furnaces the equivalent of 140,000 cub. ft. of producer gas at N.T.P. at a temperature of 300° C. This gas has the average composition :—

	Per cent.
CO_2	6·0
CO	24·0
H_2	8·8
CH_4	2·4
N_2	58·8
	100·0

and a calorific value of 130 B.Th.U. = 72·3 C.H.U.

Heat Supplied.

Heat of combustion of producer gas	140,000 × 72·3	= 10,111,100 C.H.U.
Sensible heat entering furnace 140,000 × 0·074 × 0·24 × 2·85		= 708,600 C.H.U.
Total heat		10,819,700 C.H.U.

(1 cub. ft. of gas weighs 0·074 lb., and has a specific heat of 0·24.) Under normal working conditions, say, to 9 per cent. of CO_2 in the burnt gas, the volume of air is given by :

$$\frac{\text{Vol. air}}{\text{Vol. gas}} = \frac{2.76}{1}$$

Then weight of air	140,000 × 2·76 × 0·08	= 30,912 lb.
Weight of gas	140,000 × 0·074	= 10,360 „
Total weight of burnt gases leaving main tower at 220° C.		= 41,272 lb.

Heat Expended.

Sensible heat in flue gas leaving at 220° C. 41,272 × 0·24 × 205	2,030,600 C.H.U.
Net heat supplied to tower	8,789,100 C.H.U.

The coal consumption per 1 ton of 65 to 92 per cent. acid may now be determined. One ton of 92 per cent. acid requires 934,100 C.H.U. (see above), to which an additional 20 per cent. is added to cover: (*a*) losses by radiation, and (*b*) losses due to dissociation of H_2SO_4 into SO_3, SO_2, etc.

$$\frac{934,100}{100} \times 120 = 1,120,900 \text{ C.H.U.}$$

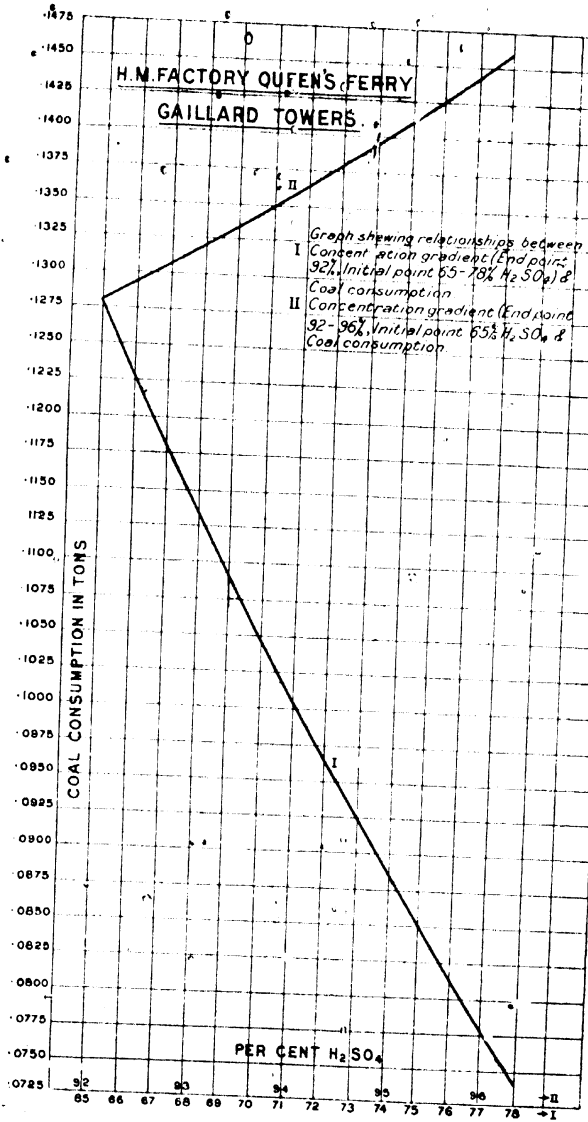
H.M.FACTORY QUEEN'S FERRY
GAILLARD TOWERS.
Graph shewing relationships between
I Concentration gradient (End point 92%, Initial point 65-78% H_2SO_4) & Coal consumption
II Concentration gradient (End point 92-96%, Initial point 65% H_2SO_4) & Coal consumption.
COAL CONSUMPTION IN TONS
·1475
·1450
·1425
·1400
·1375
·1350
·1325
·1300
·1275
·1250
·1225
·1200
·1175
·1150
·1125
·1100
·1075
·1050
·1025
·1000
·0975
·0950
·0925
·0900
·0875
·0850
·0825
·0800
·0775
·0750
·0725
PER CENT H_2SO_4
92
93
94
95
96
→II
65
66
67
68
69
70
71
72
73
74
75
76
77
78
→I
I
II

Fig. 110.

But working to a 9 per cent. CO_2 content in the burnt gases, the available heat per ton of coal for concentration in the main tower is 8,789,100 C.H.U. Hence the concentration of 1 ton of 65 to 92 per cent. H_2SO_4 requires:

$$\frac{1,120,900}{8,789,100} = 0.128 \text{ ton of coal.}$$

The value for other strengths of acid can be obtained from Fig. 110.

The influence of air dilution on the coal consumption with a constant feed and product, and assuming the dissociation of sulphuric acid to be constant, is shown in Fig. 111.

CO_2 in Burnt Gases.	Vols. Air. / Vols. Gas.	Coal Consumption.	CO_2 in Burnt Gases.	Vols. Air. / Vols. Gas.	Coal Consumption.
17·1	1·06	0·116	8·0	3·24	0·132
9·0	2·76	0·128	5·0	5·64	0·157

The coal consumption of 0·116 is that obtainable theoretically by adding just that quantity of air necessary for complete combustion of the producer gas. It is not contended from this that as high a CO_2 content as possible should be aimed at. It has been stated already that the most suitable furnace temperature to work to is in the neighbourhood of 1000°. The comparisons noted above showed the distinct economic advantage of working to a CO_2 figure of 9 to 10 per cent. as against a low CO_2 figure, say, 5 per cent., representing a temperature in the neighbourhood of 600°.

GILCHRIST CONCENTRATION PLANT.

A patent has been taken out by the Chemical Construction Co., and P. Gilchrist[1] (U.S. P. 1195075 of 1916; B. P. 103993 of 1917), for an improved concentrator which consists of a combination of the Kessler saturex with a packed Gaillard tower as recuperator. A detailed description of the plant, as

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[1] *J. Soc. Chem. Ind.*, 1916, p. 1015; *ibid.*, 1917, p. 647.

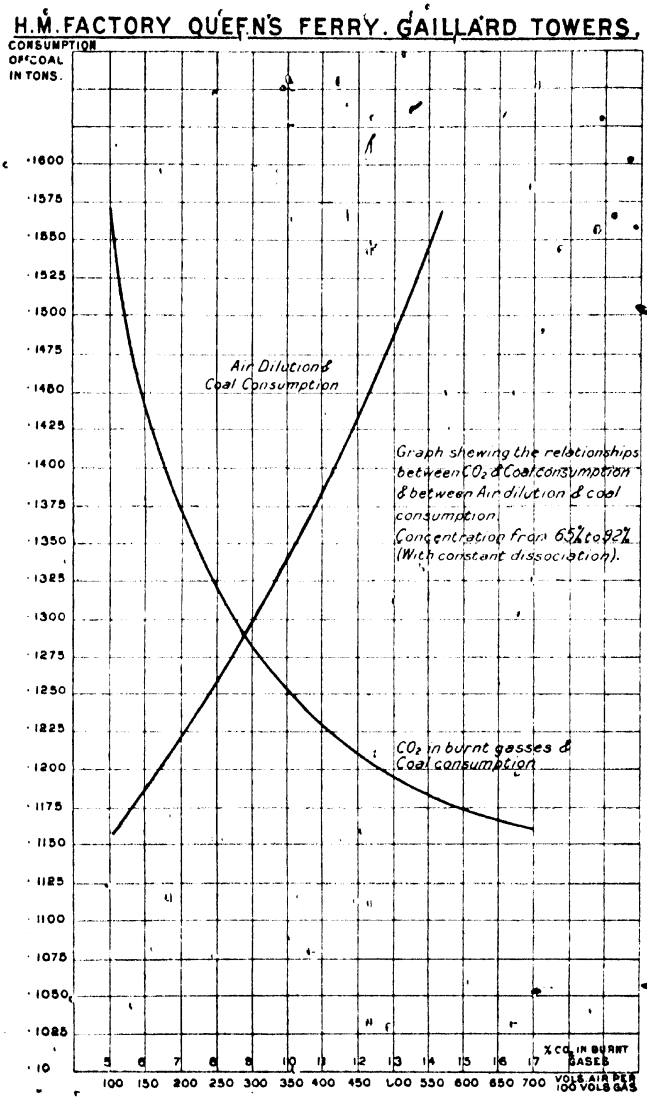

H.M. FACTORY QUEEN'S FERRY. GAILLARD TOWERS.
CONSUMPTION OF COAL IN TONS.
·1600
·1575
·1550
·1525
·1500
·1475
·1450
·1425
·1400
·1375
·1350
·1325
·1300
·1275
·1250
·1225
·1200
·1175
·1150
·1125
·1100
·1075
·1050
·1025
·10
5 6 7 8 9 10 11 12 13 14 15 16 17
% CO₂ IN BURNT GASES
100 150 200 250 300 350 400 450 500 550 600 650 700
VOLS. AIR PER 100 VOLS GAS
Air Dilution & Coal Consumption
CO₂ in burnt gasses & Coal consumption
Graph shewing the relationships between CO₂ & Coal consumption & between Air dilution & coal consumption.
Concentration from 65% to 92%
(With constant dissociation).

FIG. III.

erected at H.M. Factory, Queen's Ferry, is given in *Technical Records of Explosives Supply*, No. 3, pp. 54-63, from which the following information is taken.

The general arrangement of the plant is shown in Figs. 112 and 113.

Each tower is fed through a series of lutes in the lead cover from an overhead lead-lined feed tank, 10 ft. by 15 ft. by 4 ft. 6 in., into which the acid is raised through a lift of 73½ ft., either by Kestner elevators or by means of pumps. The acid is concentrated as it flows through the packing of the tower, and delivers into a pan or saturex, where further concentration is effected, finally being delivered through coolers to the main storage tanks as concentrated acid. The gases are led from the main tower through a quartz-packed scrubber to a 21-in. Kestner fan, and thence to the stack, or, in the final arrangement of the plant, to the Cottrell precipitator. Two independent units were installed, each capable of concentrating 70 short tons of 93·5 per cent. sulphuric acid from 65·6 per cent. acid, or 35 short tons of 97 per cent. sulphuric acid from 65·5 per cent. acid, using in both cases 162,000,000 B.T.U. per twenty-four hours, or approximately 1,000,000 cub. ft. of producer gas.

The furnace consists of firebrick structure, sheathed in steel. The gas is led from the main producer flues to the entrance of the furnace, by two gas-flues, 2 ft. by 3 ft., and is burned with the admission of primary air in a combustion chamber, 8 ft. 11 in. by 11 ft. 5 in. by 5 ft. 3 in., which is surmounted by a false arch, over which secondary air is admitted. The products of combustion enter an up-cast 8 ft. by 4 ft. 6 in. by 11 ft., filled with chequer brickwork, and are delivered to the saturex by a cross connecting flue, 4 ft. 6 in. by 5 ft.

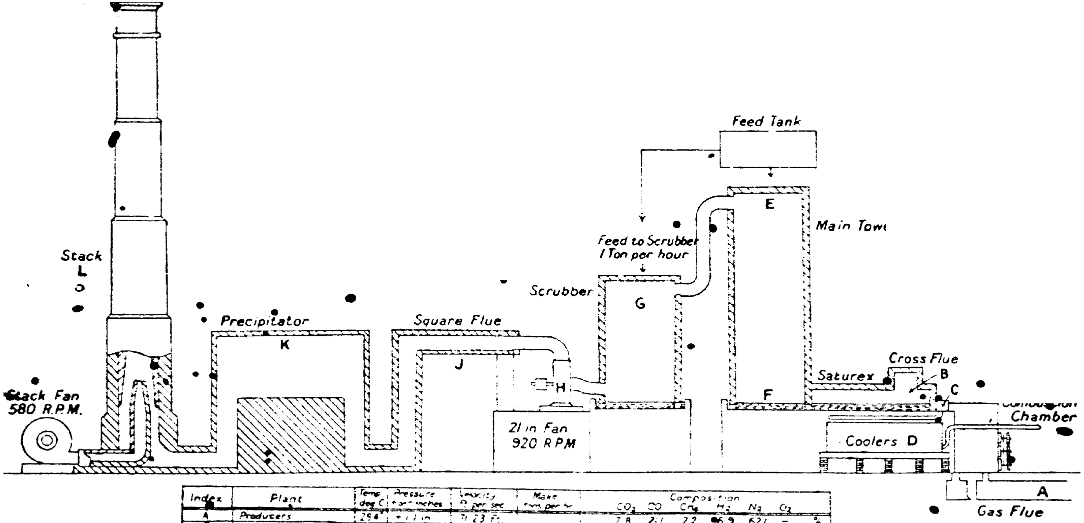
Saturex.—The saturex consists of a 20-lb. lead pan, 37 ft. 7½ in. long by 9 ft. wide by 18 in. deep, lined with three layers of 2-in. acid-proof tiles set in silicate cement, and covered with a firebrick arch fitted with four transverse baffles, which deflect the hot furnace gases on to the surface of the acid. The whole structure is built on concrete foundation, 9 ft. above the floor level, in order to give a gravity flow to the coolers and tanks. The sludging hole and acid run off are fixed so that a layer of acid 7 in. deep remains always in the bottom of the saturex. To facilitate concentration, the acid is agitated by means of a series of compressed air-jets. The concentrated acid, at a temperature of 250°, flows from the run-off pipe into a brick-lined conduit leading to a cooler which is capable of cooling 100 tons per twenty-four hours from this temperature down to 35°.

Main Tower.—The inside dimensions of the main tower are 11 ft. square and 47 ft. 3 in. high, and the tower is erected on a base of acid-proof tiles inside the same lead pan as the saturex. The tower is built up of acid-proof bricks set in special acid-resisting cement, with walls 18 in. thick and lined with a 4½-in. inner wall of acid-resisting tiles for the first 14 ft. The packing rests on seven arches, sprung from the sides of the tower, and is arranged as follows: (*a*) 14 ft. of chequer brickwork 3-in. spaces; (*b*) 7 ft. 10 in. of chequer brickwork 2-in. spaces; (*c*) 10 ft. of 4-in. quartz; (*d*) 4 ft. 3 in. of 3-in. pottery rings.

Scrubber.—From the tower the gases pass through a 36-in. lead off-take into a scrubber, 31 ft. 6 in. high, built inside a 15-lb. lead pan, with 18-in. walls of acid-resisting brick. For the first 13 ft. 3 in. there is an inner lining wall, 4½ in. thick, which is reduced to a 1½-in. lining tile for the remainder of the height of the scrubber. The internal cross section is 15 ft. 1½ in. by 12 ft. 10½ in. at the base, increasing to 15 ft. 10½ in. by 13 ft. 7½ in. above the top of the inner wall. The packing rests on chequer brickwork, and consists of the necessary layers of 10-in. and 6-in. quartz, to carry the main filling of 2-in. quartz, the total packing weighing about 300 tons. Both the lead off-take from the main tower and the scrubber are sprayed with weak acid, to cool and scrub the gases.

Fans.—The draught through the plant is produced by means of a 21-in. Kestner high-pressure fan similar to that described on p. 228. Up to the time when the plant was shut down, the fumes were passed from the fan to the stack, but the final arrangement included further scrubbing in a Cottrell precipitation plant (see p. 269).

Results.—The figures given in table on p. 244 show the conditions obtaining for an average day's working.



Index	Plant	Temp deg C	Pressure + or − inches	Velocity ft per sec	Make tons per hr	Composition CO₂	CO	CH₄	H₂	N₂	O₂	
A	Producers	294°	+ 1.1 in	71.23 Ft.		7.8	21.1	2.2	6.9	62.1	–	%
B	Cross Flue	790°	+ 0.3 in			7.8	–	–	–	–	12.3	%
C	Saturex overflow	258°				93.6 % H_2SO_4						
D	Coolers	23°			3.1 tons	93.8 % H_2SO_4 @ 23° C						
E	Main Tower Top	120°	−0.46 in	11.46 ft	3.75 tons	70.3 % H_2SO_4 @ 23° C						
F	Main Tower Bottom	235°				88.9 % H_2SO_4						
G	Scrubber	104°			2.1 tons	57.2 % H_2SO_4 @ 73° C						
H	Fan	101°	−1.37 in	51.75 ft		Total acidity as SO_3 1.37 gms per 100 litres						
J	Square Flue	85°	see Graph for same	20.02 ft								
K	Precipitator				too small to measure	33.0 % H_2SO_4 @ 62° C						
L	Stack	45°	+ 0.59 in	10.01 ft.		Total acidity as SO_3 0.32 gms per 100 litres						

FIG. 113.

	Tons.	Percentage Composition.	Temperature.
Feed acid to main tower	131·45	70·30	23° C.
Concentrated acid produced	78·94	93·80	258° „
Weak acid run into scrubber	21·75	48·46	36° „
Weak acid ex-scrubber	47·30	57·20	79° „
Temperature at main tower off-take	...	...	117° „
„ „ fan	...	...	100° „
„ „ base of stack		...	63° „

General Conclusions.—The excessive wear and tear on the base of the tower and saturex has been the most serious trouble experienced. The temperature of the acid in the saturex causes the lining tiles to expand and lift, thus forming a channel way through which the hot acid attacks the lead base. As soon as this is eaten through, the concrete base is attacked, and whenever a leakage of this kind occurs, it necessitates taking up the whole of the tiling and renewing the whole or part of the leadwork. Careful control of the temperatures of the furnace and the acid in the saturex decreases the trouble, but does not entirely overcome it. A further difficulty is due to the settling of the sludge in the feed acid in the saturex, which requires to be cleaned out about once a month, by which time the whole of the saturex is full of sludge. Even when no repairs are required, this necessitates the thorough cooling down and draining of the plant before the saturex is washed out

Some particulars are taken from the "Report on the Statistical Work of the Factories Branch," issued by the Department of Explosives Supply of the Ministry of Munitions (see pp. 245 and 246).

According to Bulletin No. 184 of the Bureau of Mines, U.S.A., p. 137, the plant consists of a combustion chamber, a concentrating flue, concentrating tower, filter and scrubbing tower, all of which are constructed of acid-proof masonry, well braced with steel framing, and supported on concrete or brick foundations at a suitable height above the ground level. On top of the concrete foundations masonry-lined lead pans are used, on which are built the masonry walls. The concentrating tower is packed with chequered brick, quartz, or other suitable packing, and the filter tower is packed with 3-in. special rings. Fuel oil, natural gas, or producer gas is used to generate the

H.M. Factory, Queen's Ferry.
Monthly Report.

Month ending 6 A.M., 29th December 1917.

GILCHRIST PLANT RECORD.

Sulphuric Acid Concentrators (N.C.).

Units Working, 1·3.

Charged.	Tons.	Per cent. H_2SO_4.	Tons H_2SO_4.	Tons SO_3.	Produced.	Tons.	Per cent. H_2SO_4.	Tons H_2SO_4.	Tons. SO_3.
Sulphuric acid	2408·0	78·42	1958·9	1598·9	Sulphuric acid (strong)	1856·2	92·08	1709·2	1395·3
Fuel—									
Coal used	218·2								

Lost.

Sulphuric acid—	Tons.	Tons SO_3.
Total H_2SO_4 charged to plant	1958·9	1598·9
Total H_2SO_4 recovered	1709·2	1395·3
Amount lost	249·7	203·6

Per cent. lost, 12·75 per cent.

Stocks.

	Tons.	Per cent. H_2SO_4.	Tons H_2SO_4.	Tons SO_3.
Stock denitrated acid on 1st December	396·7	78·4	311·1	254·0
Stock concentrated acid	14·0	91·9	12·9	10·5
Stock weak sulphuric acid	61·7	73·0	45·0	36·8
Denitrated sulphuric acid received, stills	2713·0	78·09	2118·7	1729·4
Weak sulphuric acid received, cascades	93·8	88·69	83·2	67·9
Total	..	...	2570·9	2098·6
Concentrated acid issued to mixing plant	1878·1	92·09	1729·6	1411·8
Sulphuric acid issued to cascades	61·9	78·19	48·4	39·4
" "	...	...	...	...
Stock of denitrated sulphuric acid on 29th December	302·1	77·8	235·0	191·8
Stock of weak sulphuric acid	...	...	48·1	39·3
Lost in sludging tanks and leaks at base of tower	...	...	260·1	212·7
Lost in concentration	...	...	249·7	203·6
Total	...	...	2570·9	2098·6

Physical Data, etc.

GASES.	Pressure. Inch. (water).	Temperature °C.	CO.	O_2.	Grams H_2SO_4 per 100 litres.
Leaving producers	1·0	...	25·3	4·2	...
Entering furnaces	0·8	370·1	24·9	7·3	8·6
" tray	...		...	8·5	8·2
Leaving tower	0·7	158·3	...	...	...
Entering fan	2·0	100·3	...	...	...
Entering precipitator	0·6	66·0	...	...	...

ACIDS.	Per cent. H_2SO_4.	Temperature °C.	Tons.		
Charged to towers	72·93	45·2	...	...	...
Leaving trays	92·08	164·3	101·3	...	...
" scrubbers	46·9	26·2	...	...	...
" precipitator	48·6	59·4	...	...	...
" coolers	92·08	17·3	...	...	...

ELECTRICAL DATA.	Amps.	Volts.	K.W. Hours.
Power consumed by Cottrell fan	570	440	6018

GENERAL.	
Tons concentrated per tower (H_2SO_4, 92·08 per cent.)	84·4
Coal used per ton of H_2SO_4 produced	0·128 ton
" " water evaporated	0·556 "
Water evaporated per unit per 24 hours	30·1 tons
Grams H_2SO_4 per 100 litres in exit gases	0·557

hot gases for evaporation. These gases pass from the combustion chamber through the concentrating flue and then up through the concentrating tower, where they come in contact with the weak descending acid, which is thus preheated and partly concentrated. From the top of this tower the gases are drawn at a temperature of about 220° F., and are led through a lead or stoneware flue to the top of the filter and scrubbing towers. An exhaust fan placed at the base of the scrubbing tower draws the gases through this tower and discharges them into the atmosphere. In flowing through the concentrating flue the gases pass over a pool of acid, which is agitated violently by forcing compressed air through it from perforations in a pipe running submerged in the acid and lengthwise in the flue. Thus a large area of acid is exposed to the direct action of the hot combustion gases. In passing up through the concentrating tower, the gases come into contact with a counter-current of weak acid. The tower is packed to allow a large contact surface for the gas and the acid, and the first portion of the concentration takes place in this tower. The flow of weak acid to the concentrator from an overhead tank is regulated to suit the conditions and results desired. The acid flows from the distributing pan to air-sealed lutes, which are equally distributed over the tower top and distribute the acid uniformly over the upper surface of the packing. In the filter and scrubbing towers, the acid mist carried over by waste gases from the concentrating tower is to a large extent recovered, though not entirely so. The loss may be 2 to 4 per cent. of the total acid. The hot concentrated acid from the concentrating flue is drawn off into lead coolers. All iron salts deposit in the flue and in no way interfere with the efficiency of the concentration, the iron salts being removed through suitable openings without shutting down the concentrator. The chemico concentrator requires about 13 to 14 galls. of crude oil to concentrate 1 ton of 93 per cent. H_2SO_4 from 62 per cent. H_2SO_4. As the gases are discharged at 200° F. or less, and the radiation loss is relatively small, the heat is fairly well utilised. These concentrators have been built in sizes having capacities of 15 to 125 tons 95 per cent. H_2SO_4 per twenty-four hours.

According to S. A. Ionides,[1] two 30-ton Gilchrist towers were installed at the British Acetones plant in Toronto, Canada, in which the coolers for the strong acid were placed below the main operating floor. The method of taking Baumé readings each hour by dipping samples from the discharge pipe of the cooler, and taking hydrometer readings from the dippers, had disadvantages, in that acid was splashed on the operator's clothes, and breakage of hydrometers was high. A simple continuous sampling device consisting essentially of a miniature air-lift with ⅜-in. lead pipe, was installed, which overcame these difficulties. For a detailed description of the apparatus, the original article should be consulted.

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[1] *Chem. Met. Eng.*, 1919, **20**, 38-9; *Chem. Abstracts*, 1919, **13**, 994.

Packed Towers.

According to Nielsen,[1] Gaillard towers packed with "Propeller" filling material (B. P. 26269 of 1913) work with good regularity owing to the recuperating property of the filling. This effect is more noticeable with an intermittent coke producer than with a continuous producer.

Klink[2] (U.S. P. 1276377, 20th August 1918) causes the weak acid to be concentrated to flow down a tower packed with inert material, through the interstices of which a counter-current of hot air is maintained. The concentrated acid is collected at the bottom, and the waste gases leaving the top of the tower pass through a condenser. The weak acid from the condenser is heated in a series of evaporating pans, and is discharged into the top of the tower.

Kilroy[3] (U.S. P. 1211594 of 1917) describes a series of towers packed with refractory material, and provided with a lead pan at the bottom. The acid is sprayed into the top of the tower, and meets the hot gases from a furnace.

Chem. Fabr. Griesheim Elektron[4] (Ger. P. 305122, 29th September 1917) describes a tower for absorbing or concentrating acid-gases, in which the gas enters at the lower, and passes out at the upper end, and is washed by a counter-current of liquid. The tower is constructed with double walls, the annular intermediate space being filled with packing, such as gravel, quartzite, etc., supported by a number of rings sloping towards the inner wall. In the annular chamber, which protects the outer walls of the tower and prevents loss of heat, the gases escaping from the inner chamber are scrubbed again by the liquid.

The Swedish Nitro Syndicate, Stockholm[5] (B. P. 10591 of 1908; Fr. P. 402078), claim the continuous production of concentrated acids in a vertical column of acid-proof material filled with pieces of similar material, heated both on the outside and inside by a current of hot gases.

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[1] *Chem. Eng.*, 5, 346.

[2] *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 654.

[3] *J. Soc. Chem. Ind.*, 1917, p. 214.

[4] *J. Soc. Chem. Ind.* (*Abstr.*), 1920, p. 393.

[5] *J. Soc. Chem. Ind.*, 1909, pp. 88, 1197.

Armstrong[1] describes a combined tower and pan system for concentrating sulphuric acid. The acid is first passed down a tower packed with quartz, where it is concentrated to 62 to 63° Be. (150 to 153° Tw.), and then through cast-iron pans set in a furnace, one above another. By the time it gets to the last pan, which is set directly on the fire, it has attained a concentration of 93 to 98 per cent. H_2SO_4. The quartz packing disintegrates rapidly, and it is necessary to introduce fresh quartz through the top of the tower. Oil fuel is used for heating, and the brick-lined tower is packed with about 4 ft. of quartz above the arches. The acid is fed in by means of a siphon and boot arrangement, so that there is about half a cubic foot sprayed over the packing once every fifty seconds. The temperature of the gas entering is about 650 to 670° C., and 138 to 143° C. leaving the tower. A strong suction must be maintained, by means of a steam jet or fan, to prevent condensation of the vapours and distillates inside the tower.

With regard to loss of acid—it is estimated that, under normal conditions when the tower is being fed with 60,000 lb. of 1·71 sp. gr. acid per twenty-four hours, the loss would be 2000 to 4000 lb. of 1·71 sp. gr. acid, whilst about 39,000 lb. of 1·84 sp. gr. acid would be obtained, and the balance—9208 lb. of 1·71 sp. gr.—would be recovered in the scrubber as acid of 1·47 sp. gr.

Kalbperry Tower.

According to Bulletin 184 of the Bureau of Mines, U.S.A., the original Kalbperry tower was first erected and put into operation about 1906, and has been in continuous service ever since. The towers are now built in various sizes and capacities by the Kalbperry Corporation of New York City. The standard tower is 5 ft. square by 39 ft. high over all, with an actual concentration height of about 25 ft. The standard tower has a capacity of 1 ton of acid per hour (141 to 167° Tw.). A typical arrangement is shown in Fig. 114. Liquid or gaseous fuel is burned in the furnace (1), the gases of combustion passing through the flues (1*a* and 2*e*) into and up through the tower (2), and to the scrubber (3). The acid to be concentrated is delivered to the supply tank (2*a*), and thence fed into the top of the tower by the automatic feeding apparatus (2*b*, 2*c*), whence it flows down over the packing in the tower against the rising hot gases, the concentrated acid flowing from the tower through the exit (5) and the coolers (6 and 7) into tank (9). The acid fumes driven off in the tower and air pass through the scrubbers (3), thence through the suction fan (11), and thence through the auxiliary scrubber (4), before being exhausted to the atmosphere at 4*c*.

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[1] *J. Ind. Eng. Chem.*, 1917, pp. 386-8; *J. Soc. Chem. Ind.*, 1917, p. 501.

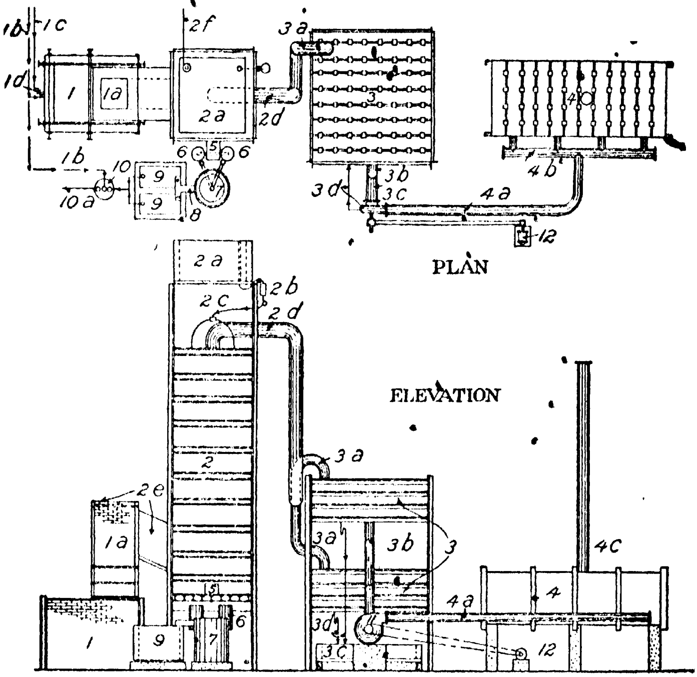

FIG. 114.

A so-called "5-foot" tower has a capacity for producing, when concentrating sulphuric acid from 141° Tw. to 167° Tw., about 1 ton of 167° Tw. acid per hour. The fuel consumption will be about 10·5 to 12 galls. of 19,000 B.T.U. fuel oil per ton of 167° Tw. acid, concentrating from 141° Tw. to 167° Tw. In addition to the concentrated acid produced, about 10 per cent. of the sulphuric acid charged is recovered as weak or scrubber acid of a strength of about 76° Tw. to 93° Tw., and there is a loss to the atmosphere of about 2 per cent. One man can easily handle a battery of four towers. Towers may be built of as large a capacity as is commercially desirable—they have been built with a minimum capacity of less than 2 tons per day—and concentration may be made from chamber strength up to 96·5 or 97 per cent., the limit of concentration attainable for sulphuric acid.

Petersen[1] (Ger. P. 302534, 23rd February 1917) utilises the waste gases evolved in the concentration of sulphuric acid as follows.

The waste gases are cooled by using them to effect a preliminary concentration of cold sulphuric acid, and are then passed into the lead chambers in place of the water or steam commonly employed.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1920, p. 688.

CHAPTER V

VARIOUS METHODS OF CONCENTRATION

Concentration of Sulphuric Acid in Vacuum-Retorts

A VERY interesting concentrating method, including the use of field tubes, formed part of an ingenious, but over-complicated system of the manufacture of sulphuric acid invented by De Hemptinne, of Brussels, and described at length, with diagrams, in our first edition, pp. 507-512, to which description we simply refer, as De Hemptinne's process has never been carried out in full, and is decidedly impracticable. Another ingenious process of his, described and illustrated in our first edition, pp. 513-516, seeks to carry out an idea previously proposed by several other inventors, *e.g.*, Kuhlmann (in 1844), viz., concentrating sulphuric acid in a *partial vacuum*, and thus reducing the temperature to such a point that the whole operation can be carried on in lead. As this process, which was actually at work for some time, has not proved successful, we also refer for it to our first edition. A further modification of his plan has been described by De Hemptinne.[1]

Of more modern forms of leaden vacuum-apparatus we shall mention that of Krell[2] (Ger. Ps. 118880, 166557, 176994; B. P. 363604; Austr. P. 21305). The acid flows through a lead pipe, *a*, Fig. 115, heated by an oil-bath, *b*. Pipe *a* is stiffened inside against atmospheric pressure by diaphragms, *c c*, leaving passages for the acid in such a manner that the acid must proceed in a zigzag course, and provided with communications in their upper part for the vapours. At the bottom of pipe *a* lies a perforated pipe, *t*, through which hot gases may be introduced for the purpose of hastening the concentration. The unperforated diaphragms, $f f_1$, stiffen the pipe and divide the steam space into three compartments, connected through h h_1 h_2 with a common vacuum-pipe, i. In this way the coolers k k_1 k_2 will condense acids of various strengths. The acid entering as chamber-acid of 100° Tw. leaves as acid of 159°

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[1] *Bull. Musée Industrie Belg.*, January 1882.

[2] *Z. angew. Chem.*, 1901, **14**, 423.

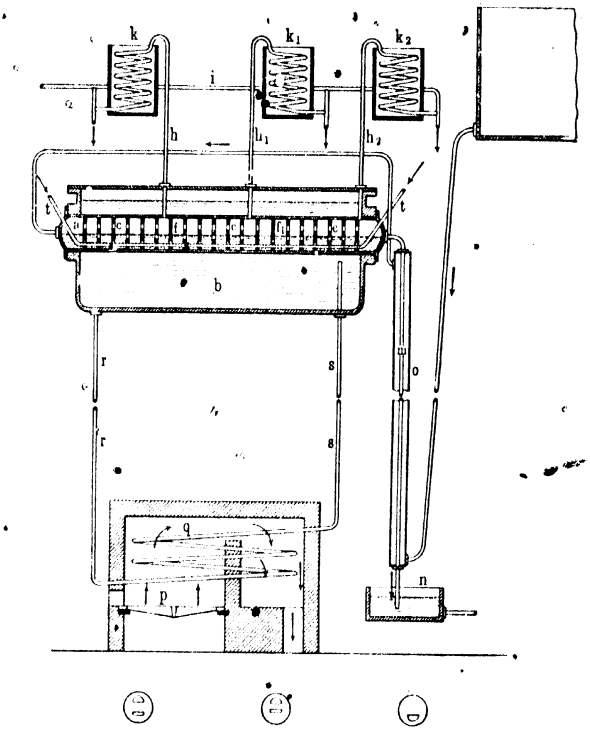

Fig. 115.

or 164° Tw. (that is, we must notice, only 86 to 90 per cent. H_2SO_4!) and descends through a pipe, *m*, which must be at least 17 ft. long, into a collector, *n*. By surrounding *m* with a jacket, *o*, the heat of the outflowing acid can be utilised for heating up the chamber-acid. Oil-bath *b* is heated indirectly by means of coil *q*, heated by a fire, *p*, and connected at both ends, *r*, *s*, with the oil-bath in such a manner that a constant circulation takes place. (According to private information, Krell employs lead alloyed with a little copper, as recommended by Lunge (Vol. I., p. 226) for higher temperatures and strengths.)

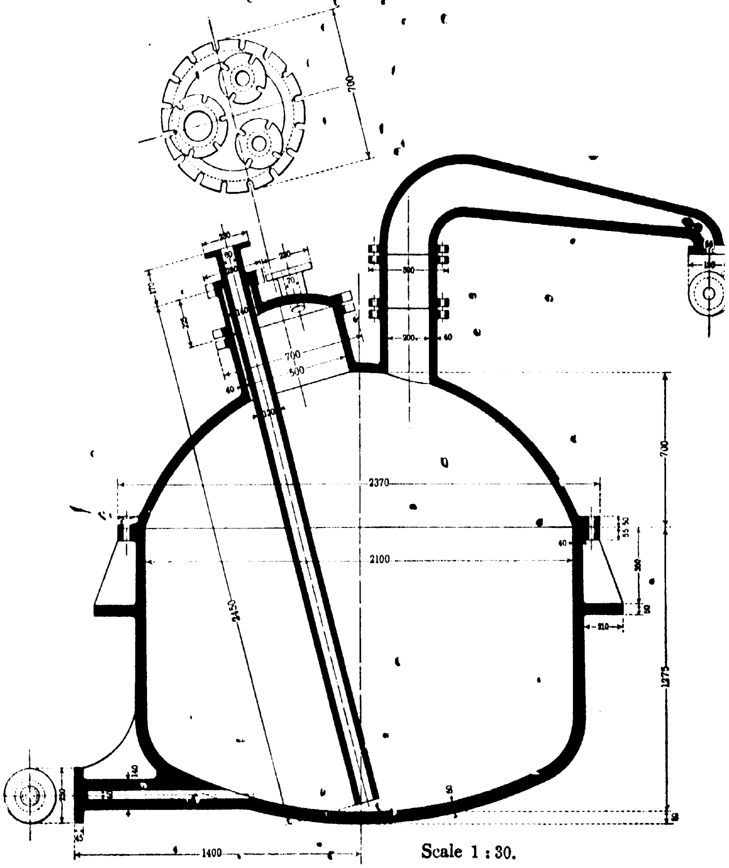

FIG. 116.

Cast-iron retorts are also used to concentrate sulphuric acid in a vacuum, starting from such strengths at which the cast iron is not yet acted upon. Fig. 116 shows the shape of cast-iron vacuum-retorts used in Germany for sulphuric acid, with great success, and furnishing very high-strength acid. Such a retort weighs about 7½ tons.

I. Meyer (Ger. P. 71580) combines a lead vessel with an iron vessel; the latter, which receives the acid in an already concentrated state, communicates with the air-pump. The pan-bottom is slightly inclined to one side. The dilute acid comes in contact only with lead, the strong acid with iron or platinum. The concentrating-apparatus is best connected with a distilling-apparatus working at the same vacuum, and continually receiving the concentrated acid through a siphon.

Brown and Georgeot (Fr. P. 241815) state a theory as to the concentration *in vacuo* in which there is nothing new.

The Kommanditgesellschaft L. Kaufmann & Co.[1] (Ger. P. 134773) concentrate sulphuric acid in a cast-iron vacuum-still by means of a steam-jacket or gaseous fuel, driving it over the heating-surface in layers of only 10 to 15 mm. depth by means of stirrers almost touching the metal, with such a velocity that the concentrated acid, by its centrifugal force, can issue continuously in spite of the vacuum. By the above treatment the steam-bubbles are more easily detached from the solid surfaces.

Cast-iron vacuum-retorts are most suitable for treating the *dirty acid* (acid-tar, sludge-acid) formed in the chemical treatment of mineral oils (*cf.* p. 289 *et seq.*). This acid, when boiled for some time, chars most of the organic substances dissolved by it, and is at the same time concentrated. But in this process much of it, sometimes nearly 20 per cent., is reduced to SO_2 (*cf.* p. 290), which causes not merely loss, but also great nuisance, unless the SO_2 can be reconverted into SO_3 (*cf.* Vol. IV.) or otherwise utilised. This difficulty is overcome by the employment of vacuum-retorts. The considerable lowering of the boiling point thus produced causes the action of the acid on the organic substance to be much less and of a different kind. There is only about 3 per cent. lost as SO_2, and the organic substance is converted mostly into a carbonaceous substance which can be removed by filtration through sand. The acid thus made is equal to 168° Tw.; it is dark coloured, but quite fit to be used over again for the refining of mineral oils.

Kynoch & Co. and Cocking (B. P. 28891 of 1896) employ

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[1] *Z. angew. Chem.*, 1902, **15**, 1098.

cast-iron retorts working with a vacuum for the concentration of waste acid from nitroglycerine.

Girod and The Gräflich von Landsberg Chemische Fabrik[1] (Fr. P. 432783; B. P. 17158 of 1911) first concentrate the acid at 150° to 160° to about 147° Tw., and then introduce it in a finely divided state into a tower or other appropriate apparatus in which a partial vacuum is maintained (preferably about 20 cm. Hg), and in which the temperature is regulated by the admission of heated air.

J. Patten[2] (U.S. Ps. 1286080, 1286188 of 26th August 1918) passes the acid to be concentrated through a series of several chambers, in which it is heated by steam coils, while maintained under a vacuum to distil off the water at a low temperature. The method of construction of the lead-work is described in detail.

The Norsk Hydro Elektrisk Kvaelstofaktieselskab[3] (Fr. P. 474995, 11th July 1914; Ger. P. appl. N15431) employs a series of vacuum apparatus on the tubular system. In the first apparatus the acid is brought up to 60 to 69 per cent., in the second to 75 per cent., in the third to 79 per cent. SO_3.

The Badische Anilin- und Soda Fabrik[4] (Ger. P. 302553 of [illegible]th January 1917) concentrate sulphuric acid in a vacuum. A heating chamber is provided, with pipes of perforated sheet iron, coated internally with lead, which is connected homogeneously to the iron at the perforations. The exterior of the pipes may also be covered with lead. These pipes resist the chemical action of boiling liquid, and also the difference of pressure. The chamber is also lined with lead, and a continuous process is practicable.

Concentration of Sulphuric Acid in a Tube System.

C. Krell (B. P. 18727 of 1894) has constructed an apparatus consisting of a cast-iron pipe, heated in a bath of molten lead, the ends being water-cooled, so that the solid lead forms a tight joint against the molten portion. Figs. 117-119 show this system with all details. One such pipe yields from 300 to 500 tons strong sulphuric acid, according to the strength of the feed acid, with one man per shift. The cleaning can be performed mostly without any stoppage of work; once in two or three weeks a thorough cleaning must be effected, which involves a stoppage of half a shift. This plan works out well for concentrating Glover acid or waste acids from nitroglycerine, etc.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1912, **31**, 127 and 335.

[2] *J. Soc. Chem. Ind.* (*Abstr.*), 1919, p. 718 A.

[3] *J. Soc. Chem. Ind.*, 1915, p. 1142.

[4] *J. Soc. Chem. Ind.* (*Abstr.*), 1921, p. 388.

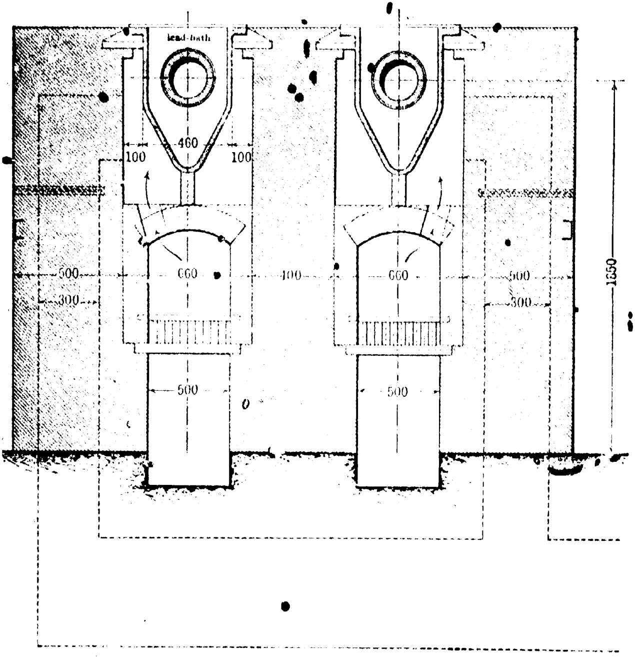

FIG. 117.

M. Liebig[1] speaks very well of it. Stolzenwald[2] gives additional details, and states that the coal consumption is 1½ tons per twenty-four hours for producing 5 tons 97 to 98 per cent. H_2SO_4. Hartmann and Benker[3] admit the success of the

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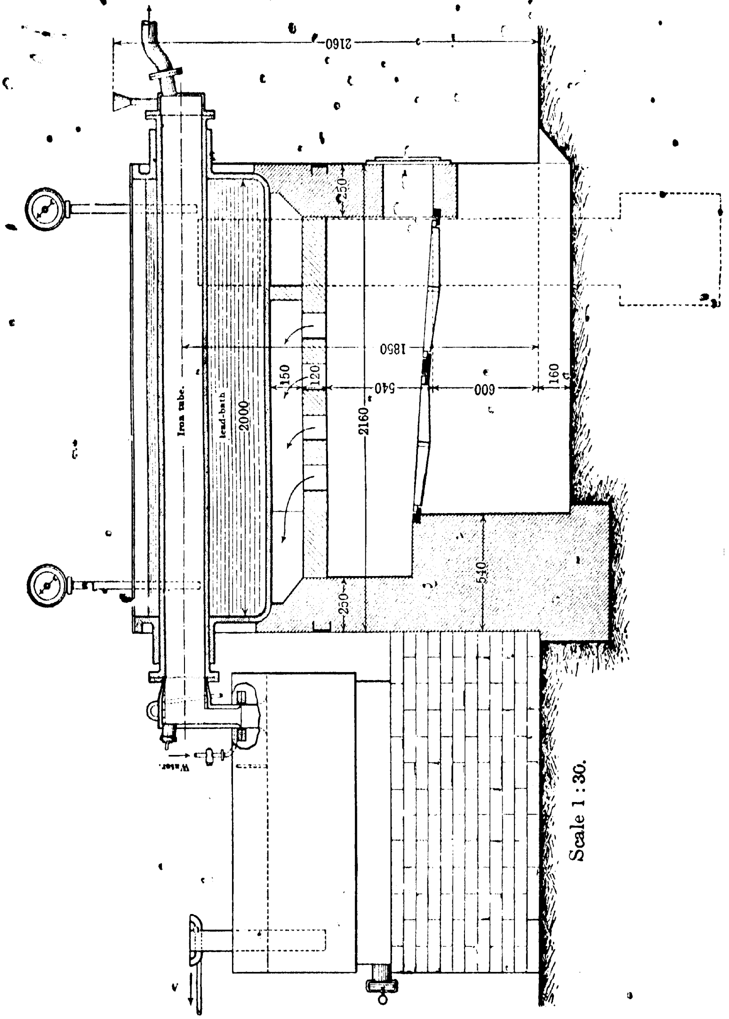
[1] *Z. angew. Chem.*, 1900, p. 184.

[2] *Ibid.*, 1910, p. 1977.

[3] *Z. angew. Chem.*, 1906, p. 565.


1850
Iron tube.
lead-bath
2000
Water.
Scale 1 : 30.

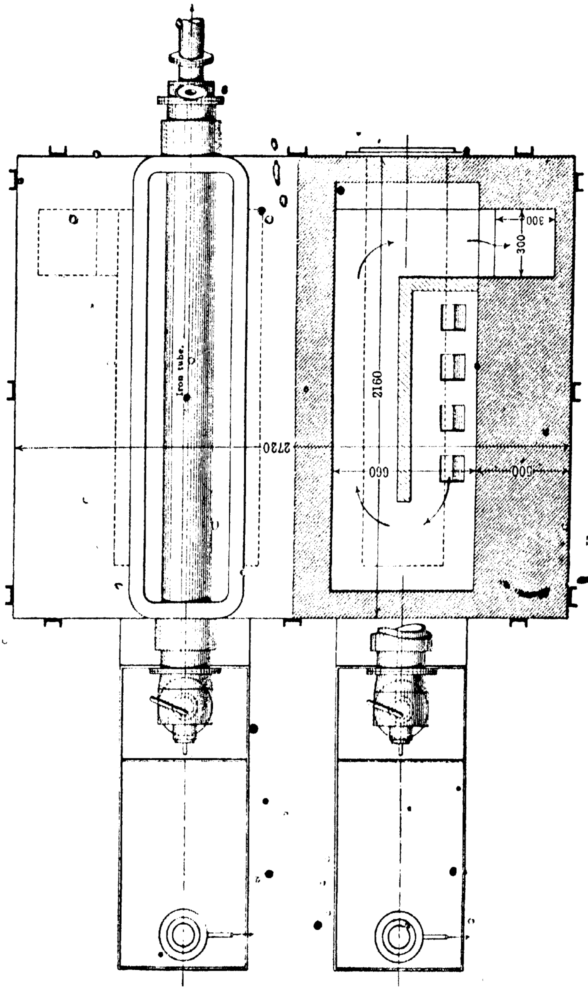


FIG. 119.

Krell apparatus, with the remark that it is more suitable for regenerating waste acids from purifying processes than for producing commercial acids. Krell's Ger. P. 166557 describes arrangements for cleaning his pipes. His Ger. P. 176944 (B. P. 4063 of 1906; Fr. P. 363604) describes a combination of inside pipes made of chilled white cast iron, in short pieces, surrounded by a jacket of ordinary cast iron.

Strzoda[1] (B. P. 26732 of 1913; Ger. P. 272158) employs for pipes serving for the concentration of acid, in the place of porcelain, etc., ordinary cast-iron pipes, coated inside with a ferrosilicon alloy (see p. 118) which is absolutely acid-proof; the unavoidable intermediate space between that coating and the cast iron is filled with an acid-proof cement, made of baryta, asbestos, Kieselguhr, and sodium silicate solution. The inventor explains his process,[2] and points out that thereby pure limpid sulphuric acid of 97 to 98 per cent. H_2SO_4 can be obtained without any wear and tear of the apparatus.

The Krell-Strzoda tube system is described in the *Z. angew. Chem.*, 1918, **31**, 185-187; *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 688 A. The concentrating tubes and certain other parts are made of an acid-resisting iron, enclosed in a shell of cast iron, the intermediate space being filled with an acid-proof cement, which seals any cracks which may appear in the brittle acid-resisting iron during use. The concentrating tubes are arranged on the slightly inclined bed of a furnace. They are connected with each other and with the distillate receiver in such a manner that the acid passes from the first tube to the second, and so on, through the series, to the acid cooler and receiver. The distillate is taken from the top of a crescent-shaped bend in the connection between each two tubes, to a cooler and receiver. Advantages claimed are: (1) working conditions easy to control; (2) comparatively short time required for the construction of the plant, and for the subsequent repairs, renewals, cleaning; (3) colourless clear pure acid.

In a small Krell-Strzoda plant of up to six tubes, the production is somewhat less than 0·9 tons of 97 to 98 per cent. per tube per twenty-four hours, and 0·9 to 1·0 per tube with more than six tubes. The coal consumption is 4 cwt. per ton of 97 to 98 per cent. Instead of condensing the distillate from the Krell-Strzoda plant in water-cooled lead pipes, H. Petersen passes the hot vapour up a small tower, in which it is dissolved by a descending stream of 50 per cent. chamber acid yielding acid of 85 to 90 per cent., which is passed again through the concentrating apparatus. The process is now in operation in several works. It is essential that the tubes be kept clean and free from slime and crustation, as, otherwise, they are burned and soon require renewal.

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[1] *J. Soc. Chem. Ind.*, 1914, p. 643.

[2] *Z. angew. Chem.*, 1914, **1**, 455.

By means of the Krell-Strzoda plans used in conjunction with a Petersen preconcentration tower, a strength of 97 to 98 per cent. may be reached from an initial 50 per cent. acid. Working to 93 to 98 per cent. concentration with an output of 10 tons per twenty-four hours, a reduction of 1·34 tons of weak acid treated is effected, as compared with other processes. Loss in this process is negligible—about 1 per cent. of very weak acid (1° B.; sp. gr. 1·007) is obtained; whereas other plants show about 10 per cent. containing an appreciable amount of sulphuric acid; which has to be recovered by reconcentration. The increased fuel consumption on the Strzoda plant—1·8 tons per 10 tons 94 per cent. acid, as against 1·2 to 1·5 tons in other plants—is counter-balanced by the higher yield of concentrated acid and smaller amount of weak acid obtained. By the employment of a ferrosilicon alloy, the wear and tear of the plant is reduced to a minimum.[1]

Brandenburg (Ger. P. 243544) employs an evaporating vessel with one or more inclined side-tubes, placed in a furnace. These side-tubes are provided with siphon-tubes inside the evaporating vessel, which produce a vivid circulation of the liquid. If they are heated, the liquid inside the vessel is heated gradually as well, and is brought to boiling. The mud settles at the bottom, without interfering with the boiling operation. The apparatus may be made of quartz, glass, or the like, as each part of it can expand without any strain being put on the other parts.

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[1] Mattenklodt, *Chem. Zeit.*, 1920, 44, 529; *J. Soc. Chem. Ind.* (*Abstn*), 1920, p. 569.

Fisher, Hall, and Moore (B. P. 27376 of 1898) let the acid run through a long cast-iron pipe, heated outside, to produce continuous concentration.

Kestner[1] (Ger. Ps. 121359, 177304; B. P. 12562 of 1906; 21548 of 1912) concentrates the acid by heating it in a perpendicular iron tube, in which it is raised to a higher level by the gas bubbles. He also concentrates the acid in perpendicular pipes, heated outside, without introducing air or gases into the liquid, by forcing this into the pipes under a pressure not sufficient for driving it up to the upper part, and compelling it to rise in thin layers along the inside walls of the pipes through the formation of vapours.

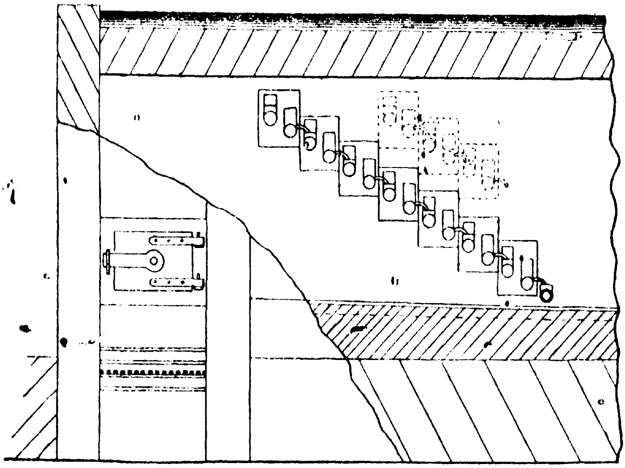

FIG. 120*f*

Harris[2] (B. P. 7728 of 30th March 1912) concentrates acid in horizontal pipes, passing at different heights through a heating flue, and its walls in such a way that they can be removed singly and replaced without interfering with the others. The pipes are closed at the ends, but are provided with an opening near one end, surrounded by a lip. The openings are disposed alternately for each pair of adjacent pipes, and at the other end

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[1] *J. Soc. Chem. Ind.*, 1913, **32**, 409.

[2] *J. Soc. Chem. Ind.*, 1913, p. 363.

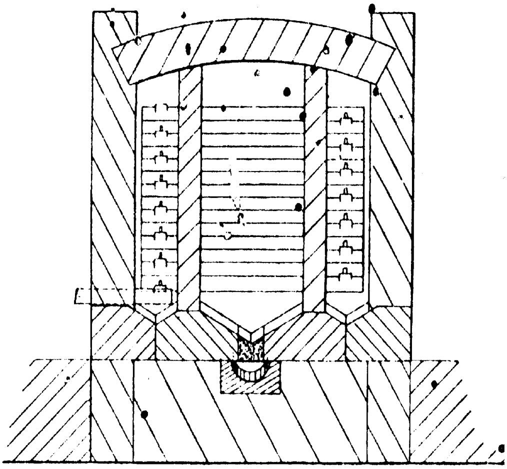

FIG. 121.

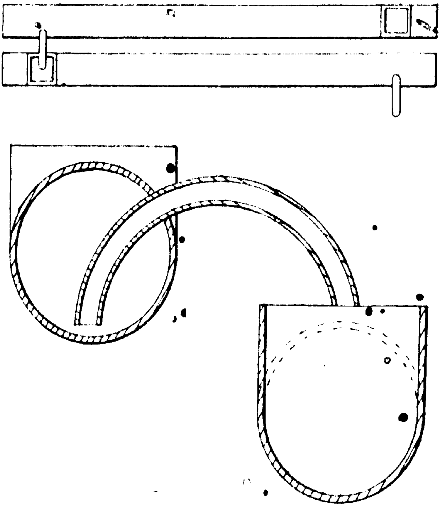

FIG. 122.

a bent tube is fixed in such a way that, before the pipes are completely full, the liquid flows into the next lower one, or, in the case of the lowest pipe, into an exit channel. The pipes are supported by the walls of a flue; the openings and tubes being outside the flue, and the middle portions extending across it. A suitable channel encloses the protruding ends of the pipes for the receipt of the vapours escaping from the openings. The flue, channel floors, and side walls are made of acid-resisting material, and provided with suitable drainage floors. The bottom of the flue floor is composed of porous bricks, which are situated over an acid gutter, so that any waste acid may be removed continuously.

Harris and Thomas (B. P. 23414 of 1914) concentrate acid in a rectifying plant consisting of a series of silica-ware tubes arranged in four tiers in a heating flue. According to the 53*rd Alkali Inspector's Report for* 1916, the "Thomas Harris" rectifying plant for making high-strength acid has undergone modification in detail, but is not yet a regular producer in quantity.

Hart[1] describes an evaporator for acid liquids, consisting of closed glass tubes 4 ft. long by 3 in. diameter, which are arranged horizontally side by side on iron supports, covered with asbestos; two or more series of these tubes are placed in steps one higher than the other, and each tube is provided with three 1-in. openings, for the introduction of the liquid and the escape of steam. The upper series of tubes discharge into the lower, and the latter into a collecting channel for the concentrated liquid. The whole system is heated by the gases from a furnace; the liquid being warmed in the first set of tubes, and then boiled and evaporated in the second set.

Concentration of Sulphuric Acid by Electricity.

Bucherer[2] makes the following calculation: The production of 100 kg. acid of 168° Tw. from 117 kg. acid of 142° Tw. requires 32,679 large calories, corresponding to—

$$\frac{32679 \times 4.2 \times 10^3}{736 \times 3600} = 44.2 \text{ electrical h.p. hours};$$

calculating the electrical h.p. hour = ½d., the above is equal to

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[1] *J. Ind. Eng. Chem.*, 1918, **10**, 555; *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 495.

[2] *Chem. Zeit.*, 1893, p. 1597; *J. Soc. Chem. Ind.*, 1894, **13**, 249.

£1 per ton (on the large scale). Further estimates of the amperage and voltage, the platinum surface, etc., must be passed over here as being entirely hypothetical.

Häussermann and Niethammer[1] have made actual experiments on this point. As might be expected, only alternating currents can be employed, since otherwise an electrolysis takes place. The concentration is very easy, but requires 1490 watt-hours per kg. This seems to exclude every possibility of practical application.

Peuchen and Clarke[2] (B. P. 24739 of 1893) propose both purifying and concentrating sulphuric (and acetic) acid by the electric current, eventually proceeding up to distillation. They propose electrodes mechanically revolving round a hollow shaft within the boiling acid. A fresh patent of theirs (Ger. P. 83526) describes stationary electrodes for the same purpose.

Wacker[3] (B. P. 3183 of 1895) proposes concentrating sulphuric acid by electricity, with introduction of SO_2.

Johnson (U.S. P. 825957) concentrates sulphuric acid containing SO_2 by an electrolytical treatment which oxidises the SO_2; more of this is constantly introduced.

Pagliani[4] describes experiments in which sulphuric acid is concentrated in vessels containing platinum electrodes. On the average forty-three kilowatt-hours were required to obtain 100 kilos of acid 1·832 sp. gr. from acid of 1·563 gr.

Taking 7500 calories as the mean calorific power of anthracite coal, the thermal efficiency—that is, the ratio of the heat theoretically necessary for the concentration of the acid to that actually consumed, is 0·25 for lead pans, 0·34 for platinum stills, 0·49 for Kessler plants, as compared with 0·93 for concentration by electrical heating. The yield by the electrical method may be increased by using closed apparatus of quartz, cast iron, or volvic lava, or preferably, enamelled cast iron, provided with a scrubber, as in a Kessler apparatus. In one series of experiments a yield of 40 kilos of acid of 1·832 sp. gr. per hour was obtained. With regard to the relative costs of the processes with coke at 60 lire (45s.) per ton, electrical energy would be 1·4 centesimi per kilowatt, and the relative costs with electrical energy and with anthracite would be the ratio of 9 to 5.

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[1] *Chem. Zeit.*, 1893, p. 1907; *J. Soc. Chem. Ind.*, 1894, **13**, 391.

[2] *J. Soc. Chem. Ind*, 1894, **13**, 251. [3] *J. Soc. Chem. Ind.*, 1895, **14**, 484.

[4] *Ann. Chim.*, appl. 1918, **10**, 134-137; *J. Soc. Chem. Ind.* (*Abstr.*), 1919, p. 171.

Matignon[1] states that during the war, owing to the very high price of coal, and the low price of electricity from water-power, acid was concentrated from 110° Tw. to 168° Tw. by electrical heating. Ferrosilicon alloys were used for the bath as well as for the electrodes.

Electrical Concentrator.

According to Bulletin 184 of the Bureau of Mines, p. 140, an electrical concentrator has been installed by the Chemical Construction Co. at Mount Holly, N.C., and has been operated intermittently for several months with good results. During 1918 a 1-ton capacity unit was installed at a chemical plant at St. Albans, W. Va. This concentrator is designed for small capacities where electrical current is available and comparatively cheap. It consists of a small bath space built of acid-proof masonry in which are placed two electrodes of acid-proof iron spaced about 2 or 3 ft. apart, the electrodes being adjustable. The bath of acid is also so arranged that the level may be lowered or raised. There is a dam of acid-proof masonry between the electrodes. The weak acid is fed in at one end of the furnace near the electrode and flows over the dam

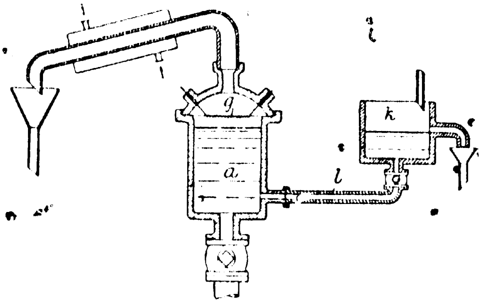

FIG. 123.

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[1] *Chem. Ind.*, 1919, p. 1301.

to an outlet at the other end. The electric current between the electrodes passes through the thin layer of acid flowing over the dam and heats this thin layer to the point where the water is evaporated at a rapid rate.

Chemische Fabrik Weissenstein-Ges., Weissenstein, Carinthia[1] (B. P. 162685. Convention date 21st May 1920), describe a plant for distilling sulphuric acid (Fig. 123). The stills are heated internally by electric heaters above the surface of the liquid. A stoneware still (*a*) connected by a pipe (1) to a supply tank (*k*) arranged to maintain a constant level, is fitted with electric resistances (*g*) of platinum, or of metals such as iron or nickelin, which are not acid-proof, but become protected by a layer of oxide or sulphate, heated by a passage of continuous or alternating currents. Reflectors of quartz, etc., may be placed above the heaters.

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[1] *Chem. Trade J.*, 23, 7, 21.

CHAPTER VI

THE CONDENSATION OF SULPHURIC ACID VAPOURS

CONDENSATION BY ELECTRICAL MEANS

ONE of the most important and promising developments in recent years is the application of electricity to the condensation of the vapours evolved in the concentration of sulphuric acid; the fundamental principles on which the method is based are given briefly below.

According to modern theories of electricity, an electric current is a stream of electrons carrying positive and negative charges, and a body through which the electrons pass freely is termed a conductor. A gas may become a conductor of electricity under the influence of various agents, such as radium, ultra violet rays of certain wave length, X-rays, etc., and is said then to be ionised. When in this state, if it is subjected to the influence of an electric discharge, the negative and positive ions begin to travel towards the electrode of opposite polarity, where they deliver up their charge of electricity. By raising the potential of the electrodes to a sufficiently high degree, they may serve also as ionising agents. In this case, if the gaseous ions encounter any solid or liquid particles in their passage through the electrostatic field, they impart a charge of electricity to the particles, which are then driven towards the electrode of opposite sign, where they are deposited. The discharge of electricity, and therefore the rate of ionisation, is facilitated from sharp points or edges, so that the "discharge electrodes" are made usually of this form, while the "receiving electrodes" are formed of curved or flat surfaces. The discharge of electricity from points gives rise to what is termed an "electric wind" blowing from the electrode, due to the repulsion between the electricity concentrated on the points and that which they impart to the surrounding air, by conduction. The air adjacent to the point of discharge receives a charge of electricity and is repelled instantly and its place taken by uncharged air. It is the rapid convection currents which are set up in this way that carry the charge of electricity to any particles, solid or liquid, with which they come in contact, causing them to travel towards the receiving electrode.

In practice, two types of apparatus are used: (*a*) Pipe treaters, in which the gases are passed through metallic tubes at a velocity not exceeding 12 ft. per second. Each of the tubes forms the receiving electrode, and the discharge electrode is provided with a thin wire stretched along the central axis of each tube, through which a unidirectional potential is applied (Fig. 124). The particles are precipitated on the walls of the tube, whence they are drained, if liquid, whilst, if solid, the current is shut off periodically and the dust shaken down from the tubes into bins. (*b*) Plate treaters, in which the gases are passed between rows of parallel vertical plates, serving as receiving electrodes, and upon which the particles are deposited. The ionisation or discharge takes place at sharp-edged electrodes hanging midway between the plates.

The precipitation of fumes and suspended particles by means of the "electric wind" from a pointed wire is a well-known experiment, which dates back to the beginning of the last century[1]; but no advance was made until Sir Oliver Lodge re-investigated the subject in 1882-1884, in a series of experiments to dissipate the Liverpool fogs by means of a high-tension electric discharge. In 1885, experiments were carried out on the precipitation of lead fumes at the Dee Bank Works,[2] but failed owing to the inadequacy of the electrical plant available. A series of patents were taken out in 1884-1886 in England and other countries, covering the methods employed, which have been developed in recent years by the Lodge Fume Co.

The Cottrell Precipitator.

The modern development of electrical precipitation is due mainly to Dr F. G. Cottrell in America. In 1906, while Professor of Physical Chemistry in the University of California, he investigated the removal of sulphuric acid mist from the

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[1] Hohlfeld, *Arch. f. d. ges. Naturlehre*, K. W. Kestner, Leipzig, 1824, **2**, 200-207.

[2] Lodge, *J. Soc. Chem. Ind.*, 1886, **5**, 572.

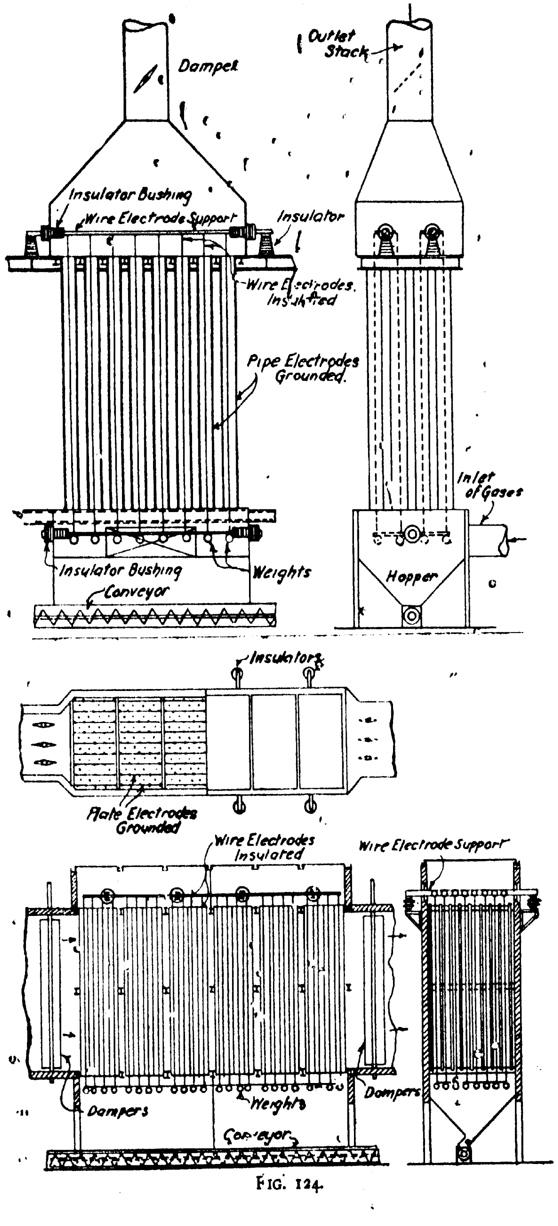
Damper
Outlet Stack
Insulator Bushing
Wire Electrode Support
Insulator
Wire Electrodes, Insulated
Pipe Electrodes Grounded.
Inlet of Gases
Hopper
Insulator Bushing
Weights
Conveyor
Insulators
Plate Electrodes Grounded
Wire Electrodes Insulated
Wire Electrode Support
Dampers
Weights
Dampers
Conveyor

FIG. 124.

gases of a Mannheim contact process, and repeated the early experiments of Lodge. His first fundamental experiment is described by Cottrell in a paper on "The Electrical Precipitation of Suspended Particles."[1]

While working one evening in the dark on the influence of a brush discharge on the fumes from sulphuric acid, a purple glow was noticed on the piece of cotton-covered magnet wire which carried the current to the discharge electrodes. This was due to the fact that every loose fibre, owing to its fineness and sharpness, acted as an excellent discharge point for the high potential current. Use was made, therefore, of iron electrodes, covered with hairy asbestos, in the first practical scale installation on the contact plant at the Hercules Works of the Du Pont de Nemours Co., in California. Although carried out only on a small scale (alternating current of 6000 volts), the results were encouraging and led to the first successful commercial application at the refining plant of the Selby Smelting and Lead Co., California. At this works silver is separated from the gold which it contains by dissolving in boiling concentrated sulphuric acid. The fumes from the boiling acid caused great inconvenience and nuisance in the neighbourhood, as they choked the tunnel of the Southern Pacific Railroad when the wind was blowing in a certain direction. The plant for precipitating these fumes consisted of a lead-lined box, containing lead-covered iron rods, fitted with asbestos, as discharge electrodes suspended between lead plates acting as the receiving electrodes. A unidirectional current of 17,000 volts was employed, and the sulphuric acid fumes were precipitated successfully in the form of weak sulphuric acid of approximately 50 per cent. strength.

The principle of electrostatic precipitation was extended rapidly to embrace the recovery of dust and fumes from metallurgical and smelting works, and met with striking success throughout the United States, as it solved a problem which had baffled the ingenuity of chemists and engineers for many years. Large sums of money had been expended in attempts to prevent the dust and fumes from destroying the vegetation and crops in the immediate vicinity of the works, which involved the payment of heavy damages and costly litigation processes. Not only did the Cottrell precipitator remove these troubles, but in most cases the value of the dust recovered was more than sufficient to pay for the cost of installation of the plant. Equally satisfactory results were obtained from the application of the precipitator to the waste gases of rotary cement kilns; and the potash in the dust recovered has proved an unexpected but very valuable by-product. Upwards of 150 Cottrell treaters have been installed in America and elsewhere, which handle the gases from a great variety of processes, including the cleaning of blast furnace gases, all types of metallurgical [illegible] and fumes, dust from mechanical pyrites burners, in sugar factories, and also in factories handling dried food-stuffs, such as powdered egg and milk. A comprehensive account of the development and application of the Cottrell precipitator, together with a bibliography of the literature on the subject, is given by Dr H. J. Bush in two papers,[1] which should be consulted for further information.

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[1] *J. Ind. Eng. Chem.*, 1911, p. 542.

The Cottrell process of electrical precipitation is covered by the following patents: U.S. Ps. 866843, 866844 of 1907; 895729, 945917 of 1908; 1016476, 1035422 of 1909; 1060065, 1067974 of 1913.

The patents are administered in America by the Western Precipitation Co. (1907), and also by the Research Corporation of New York formed in 1912, when Dr Cottrell became Director of the U.S. Bureau of Mines.

The International Precipitation Co. of Los Angeles, California, controls the patents' rights outside America, and the sole representatives for the United Kingdom and some of the Dominions are Messrs Huntingdon, Heberlein & Co., Ltd., of Ildesleigh House, Caxton Street, London, S.W. 1, to whom the author is indebted for drawings and information.

Recently a new company (Lodge-Cottrell, Ltd., of 51 Great Charles Street, Birmingham) has been formed in the United Kingdom to work the combined patents of Sir Oliver Lodge and Dr F. G. Cottrell.

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[1] *J. Soc. Chem. Ind.* (*Review*), p. 389; *J. Soc. Chem. Ind.* (*Trans.*), 1922, p. 21.

Other Electrical Precipitators.

Heimrod and Egbert[1] describe a tubular type of precipitator for the condensation of sulphuric acid mist, in use in a Wisconsin plant. In one of these precipitators, 3000 cub. ft. of gas per minute at 57° C. is treated from three tower concentrators (yielding 50 tons of 66° B. (93·18 per cent. H_2SO_4) per twenty-four hours), and 3000 lb. of acid of 18° B. (20 per cent. H_2SO_4) is recovered per twenty-four hours from the mist. A potential of 75,000 volts is employed, with a power consumption of 3½ kilowatts. Another unit, similarly equipped electrically of twelve pipes, each of 12 in. by 15 ft., treats 2500 cub. ft. of gas per minute at 93° C. from two tower concentrators (producing 40 tons of 93·18 per cent. acid per twenty-four hours), and 3500 lb. of acid of 33° B. (39 per cent. H_2SO_4) is recovered. One of the largest installations treats 3[illegible],000 cub. ft. of gas at 82° C. per minute from twenty-two cascade concentrators, each producing 10 tons of 93 per cent. acid per twenty-four hours. Four units, each of twelve pipes, 12 in. by 15 ft. are employed, and 25 tons of 45° B. (55 per cent. H_2SO_4) acid is recovered per twenty-four hours.

The high potential parts of precipitators for collecting acid mist must be provided with insulators having a large safety factor as regards voltage rating, and must be protected from acid fumes. Fans are used mostly to create the necessary draught, but steam jets are used in some cases, though they are not so satisfactory.

Thum[2] reviews the practical details which require attention in equipping a Cottrell electrical precipitator, and the conditions which require investigation and adjustment to obtain efficient operation. In treating fumes containing sulphuric acid, the insulators are attacked rapidly and punctured by the thin film of acid deposited on them, and their replacement is an important item in the maintenance charges.

Bush[3] gives an account of the development of the Cottrell system of electrostatic precipitation in England, and its application to the recovery of sulphuric acid fumes at H.M. Government factories. Detailed information of the plant erected at H.M. Factory, Queen's Ferry, is given in *Technical Records*, No. 3, of the Ministry of Munitions, p. 63 *et seq.*

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[1] *Chem. and Met. Eng.*, 1918, p. 309 ; *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 729.

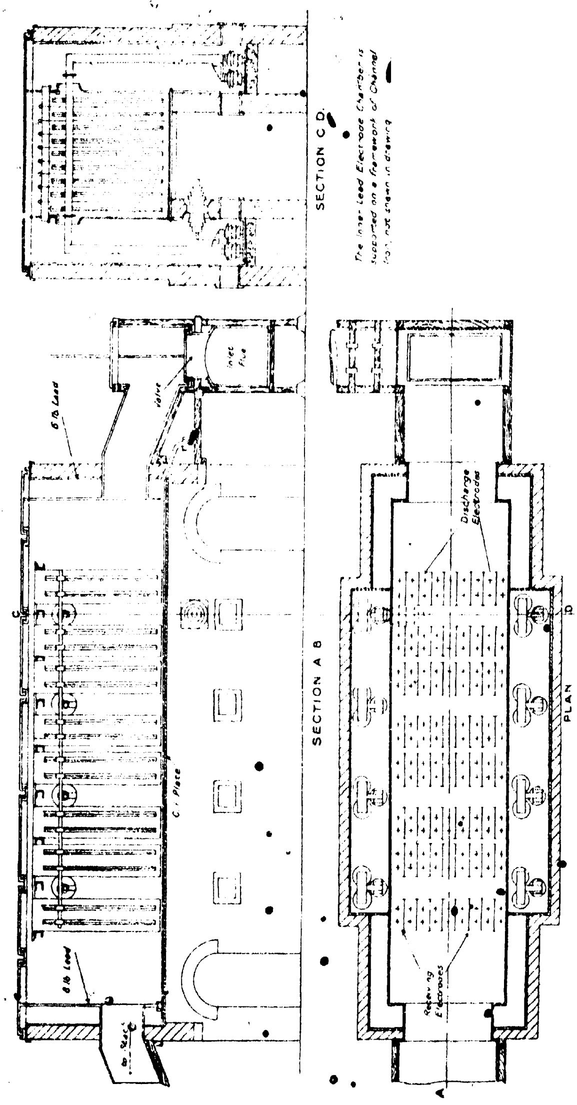
[2] *Chem. and Met. Eng.*, 1919, p. 59 ; *J. Soc. Chem. Ind.* (*Abstr.*), p. 163.

[3] *J. Soc. Chem. Ind.* (*Review*), 1918, p. 389.

The Working of the Cottrell Precipitator.

The first Cottrell plant was erected, in 1917, at H.M. Factory, Queen's Ferry, for the purpose of treating the fume from two batteries of eight Gaillard towers, concentrating the waste sulphuric acid from the manufacture of explosives. The fumes, after passing through ordinary coke scrubbers, are collected in a common lead main, and led to a precipitator divided into four compartments, each of which is designed to treat 16,000 cub. ft. per minute, the total volume being estimated at 48,000. Thus, one compartment is always kept in reserve ready for immediate use, in case one of the three has to be isolated from the rest for inspection or repairs. The gases are aspirated through the plant by means of a Davidson injector, which induces the necessary draught in the brick-built outlet stack. The injector is fitted with a 45-in. inlet Sirocco fan driven by an 80 h.p. motor, at a speed of 580 to 630 r.p.m., and is capable of dealing with 50,000 cub. ft. of air per minute. The average power consumption is 1920 kilowatts per twenty-four hours. The four treater chambers are built on a reinforced concrete foundation, in acid-proof brickwork, with removable lead-lined covers resting in lutes on the side walls. Each treater is 30 ft. 1 in. long, 7 ft. 6 in. wide, and 8 ft. 6 in. high (internal dimensions), and the whole of the base is covered with a lead tray, 3 in. deep, sloping slightly towards the discharge opening at one end.

The electrodes are of the plate-and-bar type. The lead plates forming the receiving electrodes (2 ft. wide by 8 ft. 5 in. long, made of 8-lb. lead) are hung from lead-covered M.S. bars about 10 in. apart. There are eight rows of receiving electrodes (sixty-four in all) in each chamber. The discharge electrodes are made of regulus metal bars (7 ft. 1⅝ in. long, and of cruciform cross section; the four wings being 1 in. long by ⅛ to $\frac{3}{16}$ in. thick, sharpened to promote discharge) and hang midway between the receiving electrodes. They are spaced 12 in. apart



The inner Lead Electrode Chamber is supported on a framework of Channel Iron not shown in drawing

FIG. 125.

in sets of eight, on lead-covered steel bars, carried on insulators. Each chamber is provided with 18 bars—*i.e.*, 144 discharge electrodes.

Although alternating current can be used for precipitating fogs, unidirectional current is necessary for cleaning moving gases. Each of the four chambers is connected to a 10-kilowatt high-tension generating set, consisting of 100,000 volt step-up transformer, motor, rectifier, and switchboard, there being five independent sets of each, which can be connected to any of the chambers. The average power consumption for four chambers amounts to 620 kilowatts per twenty-four hours. The electrical potential maintained between the electrodes varies from 68,000 to 73,600 volts. The bars are negative, and the plates and positive poles are earthed. The gases enter the precipitator at a temperature of 85 to 90° C. (corresponding with a fan temperature of 100° C.), and leave at 10 to 15° C. below the entrance temperature. The average velocity is about 3 ft. per second. The amount of acid recovered averages 30 tons of 51 per cent. H_2SO_4 from a total of 420 tons H_2SO_4 charged to the towers as 67·5 per cent. H_2SO_4. This represents about 3 to 3½ per cent. of the total H_2SO_4 charged to concentrators. About 1 to 1·2 per cent. of the acid passes up the stack into the atmosphere.

The installation at R.N. Cordite Factory, Holton Heath, erected by Messrs Huntingdon, Heberlein & Co., for treating the fume from Kessler concentrators is described in *Engineering*, 28th January 1921. Two chambers in parallel form a unit for dealing with the fumes from two Kessler plants, concentrating from 10 to 15 tons of sulphuric acid per twenty-four hours. The treater chambers are wooden boxes, 19¼ ft. long, 5⅜ ft. high, 4½ ft. wide, lined with 10-lb. sheet-lead, and occupy the same space as one of the old coke-packed scrubbers. The discharge electrodes are regulus metal bars, of cross-shaped section; the collecting electrodes are lead plates, made of 8-lb. sheet-lead, and are earthed. The treaters are worked generally with current at 55,000 volts. The fumes from the two Kesslers are drawn through a coke-scrubber, and enter the treater at about 80° C., with a velocity of 5 ft. per second. The weak acid recovered contains 30 to 34 per cent. by weight of H_2SO_4. By-passes are provided to allow the scrubber to be cut out, and the gases to be taken straight through to the treater, if desired.

Delasalle[1] describes the preliminary laboratory experiments and the theoretical considerations which served as a basis for the design of the plant erected for the Service des Poudres in France for precipitating the sulphuric acid mist from two Gaillard towers.

The plant consisted of sixty lead pipes of 3 mm. thickness, 20 cm. diameter, and 3 metres in length, supported at their upper ends by lead-covered iron collars, resting on the floor of the upper chamber. In order to prevent drops of liquid from entering the lower chamber, the pipes were made in two sections, of which the smaller was enclosed in the larger for part of its length; thus forming an annular space, which was expanded into a lute, into which the acid fell, and which served as a liquid seal to prevent the entry of air. From this seal the acid flowed to a collecting vessel of lead.

The electrodes consisted of wire formed like a star, and attached to lead-covered iron rods in the upper chamber terminating in leaden plates in the lower chamber. The fume was made to traverse the precipitator from top to bottom, and its distribution was effected by special devices. The apparatus was placed between the Gaillard plant and the fan, so that it was always under suction, and the connections were so arranged that it could be worked in conjunction with either or both towers, with or without the coke-box, or cut out altogether. In order to obtain acid of a strength of 40° B. (sp. gr. 1·384) maximum, the temperature at which the gases enter the precipitator must not be below 100° C., and a portion of them was therefore conducted to the apparatus direct from the coke-box to maintain this temperature. The average yield from two Gaillard towers producing 1950 kg. (100 per cent.) H_2SO_4 every twenty-four hours, excluding the coke-box acid, was 11·5 g. per cubic metre of fume—the latter having a residual acidity after treatment of 1 g. of 0·18 to 0·2 g. representing SO_2. Including the amount recovered from the coke-box, which averaged 5 g. per cubic metre, the total yield was 575 kg. H_2SO_4 per Gaillard tower per twenty-four hours.

The table on next page shows some of the results obtained.

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[1] *Chem. et Ind.*, 1920, pp. 291-316; *J. Soc. Chem. Ind.* (*Abstr.*), 1920, p. 720.

Test No.	Working Conditions.	Voltage.	Temperature of Fumes.		Acidity of Fumes.		Acid Recovered.			Percentage Recovered.
			Entering 0° C.	Leaving °C.	Before.	After.	Density in Degree B°.	Quantity in Litres per minute.	66° B. H_2SO_4 per 24 hours (in kilogs.).	
1	One Gaillard with coke scrubber	38,000	73	59	4·4	0·82	18·8	1·76	600	82 per cent.
2	One Gaillard with coke scrubber	38,000	74	60	6·8	0·9	18·8	1·80	600	87 ,,
3	One Gaillard without coke scrubber	38,000	120	60	26·2	0·99	41·0	4·8	4,850	96 ,,
4	Two Gaillards with coke scrubbers	42,000	79	72	12·0	1·0	30·0	3·24	2,050	95·5 ,,
5	Two Gaillards with coke scrubbers	42,000	85	72	13·7	1·3	30·4	3·06	1,968	90·5 ,,
14	Two Gaillard gases taken partly direct, partly through coke scrubbers	42,000	94	76	19·8	1·0	36·2	4·0	3,330	95 ,,
15	Two Gaillard gases taken partly direct, partly through coke scrubbers	42,000	100	85	23·9	1·0	40·2	4·5	4,650	95·8 ,,

The efficiency may be increased by raising the temperature, but it is reduced if the fume velocity is too high, or by the presence of nitric acid. Modifications of the plant were effected as regards increasing the pipe lengths to 3·25 metres, and the diameter to 100 mm., and the direction of the fume was reversed.

It is claimed that the use of the plant with nine Gaillard towers produced an economy of 95,000 francs per annum, and when it was also applied to the recovery of acid from seven 15-ton Kessler systems, the total gain amounted to 200,000 francs per annum.

In the table on p. 280 there are listed the electrical precipitator installations that have been erected and satisfactorily operated for removing sulphuric acid mist from gases from concentrators in America.[1] This table includes data on the number and type of towers, with their combined capacities and feed, the recoveries and concentration of the recovered acid, and essential data on the size and operating conditions of the precipitators.

Typical Operating Costs for Tower "J" for One Year.

Power (200 watts per pipe, 300 days, at 2 cents per kw.-hour)	$460
Labour, 2 hours per day at 50 cents per hour	$300
Repairs (estimated)	$200

With the exception of installations J and K, all precipitators were installed after the usual coke-scrubbing towers, and for the primary purpose of eliminating a nuisance. Installation J was made without coke scrubbers, but there was included in the system a cooling coil of 12-in. lead pipe, with return bends exposed to the air, having a total length of 125 ft. When scrubbers are omitted the addition of such a cooling coil is advisable, because the precipitator efficiency is vastly improved when the gases are not hotter than 200 to 210° F. at the time of treatment. The efficiencies of these installations have been consistently high. Continuous operation with clearances of 98 to 100 per cent. have been maintained. Where scrubbers have been omitted, tests have shown over-all concentrator efficiencies of 96 per cent., based on the amount of acid passed

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[1] U.S. Bureau of Mines, Bull. 184, p. 142.

Data on Removal of Acid Mists from Concentrator Gases by Electrical Precipitators.

Installation.	No. and Type of Concentrator[a].	Capacity Tons of 66° B. Acid per 24 hours.	Strength of Acid Feed, ° B.	Strength of Acid precipitated ° B.	Tons of Acid precipitated per 24 hours.	Tons of Acid precipitated reduced to 66° B.	Percentage of Total Acid precipitated.	Number of Pipes in Precipitator.	Volume of Gases, cubic feet per minute.	Temperature of Gases ° F.	Cost of Installation.
A . . .	1—K	16	53	16	0·72	0·13	0·8	5	1,000	150	$3,000
B . . .	2—K	43	53	16	1·6	0·3	0·8	10	2,000	150	5,000
C . . .	3—K	37	53	16	1·85	0·35	1·0	12	2,400	150	5,000
D . . .	5—K	90	50	20	15·0	3·6	4·0	32	6,000	123	14,000
E . . .	3—S	50	50	18	3·3	0·7	1·4	16	2,640	135	6,500
F . . .	1—S	40	60	33	1·75	0·7	1·8	12	2,250	206	4,700
G . . .	3—S	50-60	14·3	...	...	...	...	24	4,800	180	9,300
H . . .	1—S	30	60	22	0·7	0·2	0·6	12	3,300	180	5,000
I . . .	4—S	40	52	32	3·0	1·2	3·0	20	4,360	155	...
J . . .	2—S	22	50	30	7·5	5·01	22·7	16	2,400	220	5,000
K . . .	22—C	170	60	45	25·0	14·8	8·7	48	35,000	200	29,000

[a] K, Kalbperry towers; S, Skoglund towers; C, cascade type.

through the tower, the amount of concentrated acid produced, and the amount recovered in the precipitator reduced to the basis of 100 per cent. sulphuric acid.

Welch (U.S. P. 1289984 of 31st December 1918) converts all the dilute acid (chamber acid) into the vapour phase, and then, by cooling to a certain determined degree, a cloud of acid of definite strength is formed, and the particles of this cloud are collected by electrical precipitation. The temperatures of cooling and the corresponding strength of acid obtained are: 260 to 280° for 90 per cent. acid; 200 to 210° for 80 per cent. acid; and 165 to 175° for 70 per cent. acid. Practically complete recovery of acid is effected.

INJECTION OF WATER AND WEAK ACID INTO HIGH-SPEED FANS.

According to the *Alkali Inspector's Report* (1916, 1917) the treatment of fume developed in concentration of strong sulphuric acid received much attention, and two new methods were under trial, both of which resulted in a marked decrease of acidity of the waste gases treated. One of these was the adoption of electrical methods to remove acid spray (see p. 268); the other was the supply of water or weak acid to the fan used for inducing sufficient draught on the fume flue of cascade units. "By this simple means also a great reduction in the acidity of the gases was effected, and its adoption may rapidly extend. In both of these methods an impressive feature is the very short period of time during which the gases are subjected to the action of electric influence or fan movement."

Experiments have shown that steam is not effective in reducing the content of sulphuric anhydride in the exit gases, but that water dissolves the acid mist until it reaches a maximum strength of approximately 45 per cent. acid, after which it has no effect on the gases. The best results are obtained when the solution contains less than 25 to 30 per cent. H_2SO_4, and, under these conditions, the SO_3 content of the exit gases is reduced below 1 gr. per cubic foot. In order to carry out this idea, acid of 25 per cent. acidity from an overhead feed is injected at the inlet of the fan, so as to impinge between the rotating blades. The liquid runs from the base of the fan into a small tank, whence it is elevated to the feed tank by means of a Kestner elevator. Sufficient water is run into the circulating system to maintain the acidity at 25 per cent., and the surplus acid is run away from the plant.

Calder-Fox High-Speed Scrubber.

A new type of scrubber has been introduced by Messrs Chance & Hunt, Ltd., Oldbury, W. A. Calder, and C. H. Fox (B. P. 126320 of 9th December 1916), which is now employed extensively for the condensation of acid mist from concentration plants of varying types. The author is indebted to Mr W. A. Calder for the following particulars.

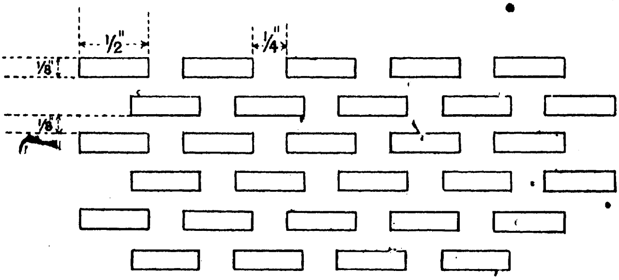

FIG. 126.

Design.—The high-speed scrubber is usually made of lead; if, however, other corrosive gases, such as nitrogen oxides, are present, the use of this metal is avoided. The exit gases from the concentrating plant, laden with acid mist, are drawn by means of a fan through a series of perforated plates, or other baffles, at a speed of not less than 20 lineal ft. per second. This causes the particles of acid mist to coalesce and fall to the bottom of the scrubber, whence the condensate is drawn off. In the *absence* of oxides of nitrogen, the lead scrubber, packed with three perforated lead baffles, is used; the plate nearest the inlet is pierced with ¼-in. holes, the second and third plates with ⅛-in. holes. The plates last four to six months, and over; the first plate is most affected, especially in the centre. In the presence of oxides of nitrogen, the scrubber is built of brick and the baffles consist either of three perforated plates made of earthenware instead of lead, or else strips of glass about 1 ft. in length,

½ ft. broad, and ⅛ in. thick, arranged as in sketch (Fig. 126). Ordinary window glass is quite suitable, and stands up well.

Temperature.—The temperature of the gases entering the scrubber should on no account exceed 130°, as the efficiency falls off rapidly at higher temperatures (probably due to dissociation); 110 to 120° is recommended as most suitable. It has been found that in the case of the Gaillard tower, the density of the condensate in °Tw. is approximately the same as the temperature in 0° C., at which condensation takes place. This holds good between 90 to 145°. If the temperature falls below 90°, the condensed acid may fall to 40 to 50 per cent. H_2SO_4. Although it is possible to water-cool the fume main leading to the high-speed scrubber, this is not desirable, as much water vapour is condensed when the gases come into contact with the cool inner surface of the main, which would remain as water vapour if the main were air-cooled.

Working of Scrubber.

The inlet damper is an essential part of the scrubber, and should be lowered so that the speed of the gases under its edge will be about 80 ft. per second. This damper spreads the gases well over the surface of the baffles, and improves greatly the working of the scrubbers. It is advisable to have two small glass windows fitted at the outlet of the scrubber, and to adjust the damper so as to obtain the clearest exit gas possible. When the right conditions obtain, ordinary print can be read with ease through a 15-in. layer of the gas. The *draught* across the scrubber and inlet damper should be about 3 in. to 3½ in. water-gauge; there is an appreciable falling off in the efficiency of the scrubber when this difference in draught falls to 2¼ to 2½ in.

Capacity of High-Speed Scrubber.

A scrubber 3 ft. internal diameter will deal with 40 to 60 cub. ft. per second; that is, with an output of 25 to 40 tons of rectified oil of vitriol per twenty-four hours, and, provided the concentration plant is run in a reasonable manner, the acidity in the exit gases can be reduced readily to less than 1 gr. SO_3 per cubic foot. The SO_2 content should be kept as low as possible, *i.e.*, under 1 gr. per cubic foot, as its presence is largely due to decomposition of the acid concentrated; and this decomposition leads to the formation of mists, very difficult to condense, and to loss of acid as SO_2.

The cost of the high-speed scrubber is only a fraction of that of an equivalent coke scrubber or electric deposition plant, whilst it is built far more quickly, and its small size enables it to be placed in positions where there is not room for a coke scrubber, and to be moved from one plant to another if desired. The simplicity of the baffles, and the fact that they can be changed in a few minutes, constitute a great improvement over the elaborate graded packing of a coke scrubber. Special technical knowledge is not required, as in the case of electric deposition plants, and the performance of the scrubber is not liable to the same fluctuations. Once the high-speed scrubber is adjusted—a matter of a few minutes as a rule—it requires no more attention than a coke scrubber, and is free from the risk of clogging, which takes place occasionally in coke scrubbers, when waste acids, containing volatile organic bodies, are being concentrated. Very few repairs are required, and a purer and stronger condensate is obtained than when a coke scrubber is used.

The following advantages are claimed for the high-speed scrubber: (1) High efficiency; (2) low initial cost; (3) small size and compactness, together with simplicity and accessibility; (4) low cost of running and repairs; (5) high strength and purity of acid recovered.

According to the 54*th Alkali Inspector's Report* (1917), a new type of scrubber, known as the "Calder-Fox" high-speed scrubber, was introduced during 1916. It is of special interest on account of the very short period of time—a small fraction o a second—in which the removal of suspended acid liquid particles is effected by frequent sudden change in direction of the flow of the gases, and by provision of surfaces so disposed as to promote friction between gas and solid. It is to be noted, however, that, in common with electrical methods, its chief effect is exerted on suspended particles, and that acid remaining in the gaseous phase is but slightly influenced. This consideration is of importance when, as is frequently the case sulphurous acid is present in important quantity. As over heating dissociates sulphuric anhydride into sulphurous acid gas and oxygen, undue pressure on a concentrating plant is apt to lead to the formation of acid in the gaseous phase, to arrest which, neither the electrical nor the high-speed scrubber seems to be suitable, unless associated with condensation of aqueous vapour by cooling. According to the 55*th Alkali Inspector's Report* (1918), the Calder-Fox scrubber was further improved in the light of accumulated experience, and is an efficient remover of suspended liquid particles.

Fires in Coke-Packed Condensers.

According to the 54*th Alkali Inspector's Report for* 1917, a scrubber connected with a cascade plant took fire. In order to prevent undue condensation of water, and so obtain a condensed acid of greater strength, the leaden casing of the scrubber was enclosed with 2-in. boarding. Various reasons were advanced as to the origin of the fire—the inferior quality of the coke packing being one of them (gas coke instead of furnace coke). This instance, however, is by no means an isolated one, similar cases having occurred in connection with Cascade, Kessler, and Gaillard plants, and no adequate explanation of their origin has been given. In one case where a wooden cover was provided and the intervening space packed with sawdust, to more effectually retain heat, it was found that the temperature of the cascade gases was sufficiently high to set the sawdust lagging on fire, although separated by the usual lead casing. Another case of internal fire was attributed to pieces of wood which had got mixed up with the coke packing. When concentrating waste acids from the manufacture of T.N.T., a certain amount of nitro bodies is carried over in the scrubber and is condensed in the pores of the coke packing. Fires have been caused in such scrubbers by the ignition of the nitro-body, due to excessive heat, such as a plumber burning lead on top of the scrubber while in action.

Fires can be caused by carelessness on the part of the plant operative, especially in the case of the Gaillard tower plant. If the supply of acid to the main tower and recuperator of a Gaillard tower is blocked for any reason, the hot furnace gases passing right through into the scrubber will drive off the weak acid and water, and ignite the woodwork and coke in a very short space of time. The supply of acid may fail on the tower, owing to:—

(*a*) The atomiser sprays or nozzles having become blocked.

(*b*) Failure on the part of the operative to change over the feed-acid eggs correctly. If the egg is blown empty, the feed will stop until this is remedied.

(*c*) Operatives have been known to throttle down the delivery valves on the feed-mains, in order to avoid changing the spray nozzles when the feed is too strong for the requisite strength of acid required. As they have no means of knowing how far they have checked the acid flow, in some cases it is shut off completely.

The box type of recuperator, fed with a constant stream of weak acid from a gravity cistern, offers greater protection against risk of fire than the open-tower type.

Reviewing the small amount of evidence which has been published on this subject, it appears probable that sufficient attention has not been directed to the fact that wood chars at a temperature of 200 to 225°; while coke does not ignite below 400° (see Mills and Rowan, "Fuel").

The temperature of the gases entering the scrubber is highest at the point of inlet, and varies between 180 to 230° according to the method of working the plant, so that, in some cases, the woodwork of the scrubber may be ignited at working temperatures. If this happens, the melting of the lead (melting-point 315°) follows quickly, and, assisted by the draught of the fan, the fire spreads rapidly to the coke packing, unless caught in time.

Comparison of Various Scrubbers.

Kaltenbach[1] examines critically various types of scrubbers in use.

Scrubbers are constructed usually in heavy woodwork and lined with brick tiles; and their dimensions are such that the surface of radiation is small in comparison with their volume, so that the cooling effect is small. Scrubbers of the type shown in Fig. 127 are irrational, because the gas encounters the bed of fine coke first, and then descends through the beds of coarser material. The gas tends to follow the path of least resistance, and descends vertically towards the exit without traversing the remainder of the packing. In a short time this section of the packing becomes choked, since all the condensation and the lead salts collect at this

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[1] *Chim. Ind.* (*Trans.*), 1921, **5**, 59.

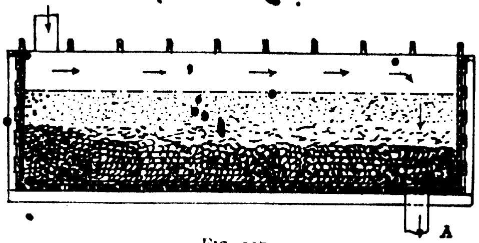

FIG. 127.

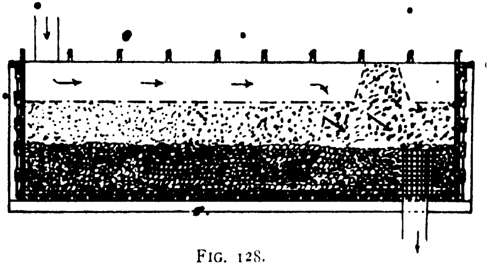

FIG. 128.

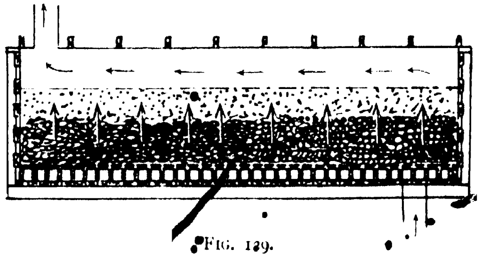

FIG. 129.

point. Fig. 128 shows a partial attempt to overcome this difficulty, by means of a barrier of fine coke, which causes the gas to take a more circuitous route. The scrubber shown in Fig. 129 is a more rational design, because the gas enters at the bottom and passes upwards through the packing, meeting first the large size packing, then the finer material, and finally the very fine layer. The gas tends to spread through the entire packing, because the resistance is uniform.

Kaltenbach recommends an arrangement of the type shown in Fig. 130. From the recuperator the gases are conveyed into a set of lead tubes, cooled externally by air, or preferably by a stream of water. The degree of cooling is regulated so that the strength of the condensed acid is such that it can be utilised on the recuperator. The first coke scrubber which follows this cooler is of small dimensions, and is designed to act, not as the big coke scrubbers to cool the gases at the same time as condense them, but solely to precipitate the liquid droplets by shock on the rough surfaces. The gases now pass into the section of the apparatus designed more especially for their purification by the condensation of the remaining sulphuric acid vapours, so that they can be discharged safely into the atmosphere. It consists of a second set of lead cooling tubes, which are regulated to reduce the temperature of the gases just to that point at which the acidity of the fumes is below the limit at which they can be emitted into the atmosphere. A second coke scrubber serves to precipitate the droplets of acid thus condensed. Kaltenbach claims that a scrubber of the above design is just as effective as the electrical precipitator for the condensation of the fumes from a Gaillard concentrating plant, and is much less costly.

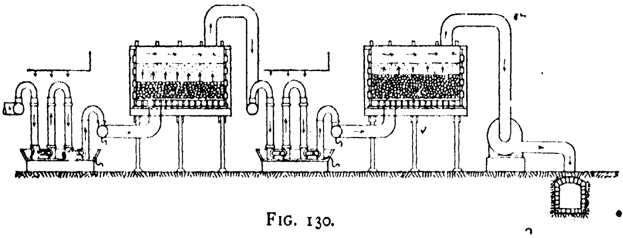

FIG. 130.

CHAPTER VII

RECOVERY OF SULPHURIC ACID FROM WASTE ACIDS

Recovery of Waste Acid from Petroleum Refineries.

THE following process serves for the concentration of acid recovered from the "acid tar" or "sludge acid" of petroleum refineries. This acid tar is first diluted with water, whereupon most of the tar is separated and skimmed off (U.S. P. of Fales, 97182 of 1867). The acid liquor is now concentrated in leaden pans, first by bottom heat and then by top heat, up to a strength of 158° Tw. The last concentration takes place in cast-iron pans with leaden hoods. The pans, two of which work together terrace-wise, are 2 ft. by 4 ft. wide and 6 in. deep; they have a rim shaped for a hydraulic lute, lined with lead, into which dips a double-walled, roof-shaped, leaden hood, through which water is kept running, on the principle of Faure and Kessler's stills (see p. 90). All the joints are made with asbestos cement. The principle of this apparatus is shown in sketch, Fig. 131.

The Chemische Fabrik A. G.[1] (B. P. 9614 of 1885) dilute the acid tar with an equal volume of water and allow to settle. The lower layer containing the acid is separated from the impurities by washing with carbolic acid, or similar bodies, and can then be employed for decomposing sodium phenate, etc. The acid is converted, preferably, into ammonium sulphate by neutralising with ammonia.

Ostrejko[2] (B. P. 18640 of 1900) describes the recovery of sulphuric acid from acid-tar by the well-known process of diluting 57° Tw., separating the tar, and concentrating 142° Tw. In order to complete the separation, the acid is again diluted with chamber acid or water, and boiled down. The removal of the tar is promoted by adding a certain description of carbon invented by the author of that communication; 1 per cent. of this is said to convert the acid into a colourless product.

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[1] *J. Soc. Chem. Ind.*, 1886, p. 160.

[2] *Chem. Zeit. Rep.*, 1902, p. 360.

U. Wedge[1] describes the usual process of working up the "sludge acid" from the petroleum refineries. As it comes from these it contains about 45 per cent. of oil. Most o this is separated by diluting the acid to 63° Tw.; it is calle "acid oil," and is utilised as fuel. The weak acid separate from it still contains 1·2 per cent. oil. It is heated in shallow, hooded lead pan, by means of a light steam-coil t 110° C., in which process a very slight quantity of sulphu dioxide is formed. The acid now enters a series of thre

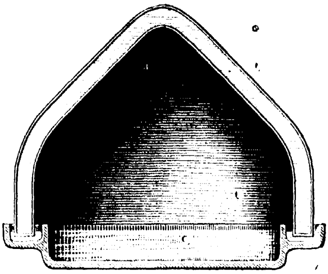

FIG. 131.

shallow lead pans, 6 ft. by 45 ft., 12 in. deep, covered wit brick arches, where it is treated with surface-fire ("weak-ac pans"). Here it gets up to 122° Tw., and a temperature 166° C., with some loss of SO_2 and SO_3 (the gases showe 1·24 gr. SO_2 and 0·92 gr. SO_3 per cubic foot). Now th acid enters a series of two lead pans of the same size as th above, and at last two iron pans, 3 ft. by 7 ft., 9 in. deep. Th lead pans are also housed in brick, and heated by surface-fi From these ("strong-acid pans") the acid issues with temperature of 230° C. and shows 166° Tw., equal to 92½ p cent. acidity. The gases from these pans showed 28·7 g SO_2 and 4·9 gr. SO_3 per cubit foot. There was a tot loss of 25 per cent. of the acid—91 per cent. of which occu in concentrating from 126 to 166° Tw.—86 per cent. bei caused by the action of the oil on the sulphuric acid formi sulphur dioxide, which cannot be removed in consequence of the heating by surface-firing. Calculation shows that 1 lb. of the hydrocarbon dissolved in the oil will destroy 20·88 lb. acid of 92½ per cent.

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[1] *J. Soc. Chem. Ind.*, 1899, p. 345.

Waring and Brackenbridge (U.S. P. 643578 of 1900) purify sludge acid by heating with about 4 per cent. sodium nitrate at a temperature of 15 to 82° C.; 1 per cent. $NaNO_3$ suffices for removing offensive odours.

Friedland and Ljubobarsky (Rus. P. 6631) dilute the acid tar, skim off the tar, allow to settle, and submit the clear liquid, brought to 106° Tw., to the electric current, which oxidises the carbonaceous matter to CO_2.

Fleischer (Ger. P. 182246 of 1906) puts the acid-tar in porous earthenware vessels, which are placed in water; pure sulphuric acid diffuses through the earthenware into the water, and the tarry substances accumulate inside the vessel, up to a maximum. The water outside is ultimately converted into acid of about 1·52 sp. gr.

Blacher and Sztencel (U.S. P. 956276) obtain pure acid from the sludge acids of petroleum refineries by running it into boiling concentrated sulphuric acid, blowing air through this and condensing the escaping vapours (*cf.* p. 292, the report of Wispek on the patents of the Steaua Romana Petroleum Co.).

Stolzenwald[1] (Ger. Ps. 212000 and 213589; Austr. P. 42408) introduces the waste acids, of whatever origin, in the crude state, or diluted with water, or preheated, at the bottom of upright, annular boiling pipes, provided at the top with outlets for gases, and for the concentrated acid, and arranged in such a manner that the temperature gradually increases from the bottom upwards. In the lower, cooler part of the pipe the oily matters are separated by the effect of concentration; in the hotter, upper part of the pipe the resins and tars and a little of the sulphuric acid are decomposed. The final products are oils, sulphuric acid, SO_2, and carbon. The latter is carried along by the acid, and is separated from this by subsidence or filtration. The gasified oils and SO_2 escaping at the top are separated by cooling, and the SO_2 can be worked for sulphuric acid. Before passing the waste acid through this apparatus, it may, after treating it with water and preheating, be treated in such a manner that the escaping oils are recovered by cooling, while the resins and tars are separated on the surface of the acid as a solid paste, leaving behind a sulphuric acid of about 106° Tw.

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[1] *Cf.* also his statements in *Chem. Zeit.*, 1908, p. 1017.

Donath[1] describes the very well-known plan of utilising waste sulphuric acid (from petroleum refining, etc.) by heating to about 300° with nitrogenous substances, such as leather, hair, etc.; by extracting the product with water, ammonium sulphate is obtained, and the residue may be utilised for decolorising purposes, or for producing potassium ferrocyanide.

Wispek[2] discusses the utilisation of the waste acids from the refining of petroleum. Two classes of such "acid-tars" must be distinguished, viz., those produced in the refining of petroleum-naphtha ("benzin") and lighting oil, and those from the refining of lubricating oils. In refining benzin or petroleum, about 10 per cent. of the sulphuric acid is decomposed, and 90 per cent. remains behind, mixed with so much organic substance that for each 100 parts of fresh acid of 168° Tw. used in the refining process, 125 to 130 parts waste acid of 106 to 120° Tw. are formed. By diluting this with water to about 64° Tw., most of the organic substance (say 20 to 25 per cent. of the waste acid) is separated in the form of a black repugnantly-smelling tar, sp. gr. about 0·900, boiling principally between 100 and 200°, and containing about one-third neutral oils and two-thirds compounds of an acid nature. The whole of the sulphuric acid collects at the bottom in the form of brown, clear, dilute acid, which must be concentrated. In the waste acid from refining lubricating oils, the proportion of sulphuric acid is about 80 per cent.; it is even in the warm state a thick liquid, from which the resinous matters are not easily separated. This acid-tar is partly freed from sulphuric acid by heating in large cast-iron pans by means of direct steam, sometimes also by a coal-fire from below, so that part of the sulphuric acid is driven out; the tarry matter remaining behind is burned under the oil-pans. The recovery of *pure* sulphuric acid of 168° Tw. from these acid-tars has not been until recently successfully accomplished, in spite of many attempts; the acid obtained was always black, and always retained injurious organic compounds. According to the process of Pilat, Bolland, and Selcer (Austr. P. 31595 of 1907), or Julius Fleischer (Ger. P. 182246, *supra*, p. 291), it is indeed possible to obtain a water-white, dilute sulphuric acid, free from tar, by submitting the acid-tar to diffusion with water through a porous diaphragm. But that white, dilute acid contains all the organic and sulpho-acids, which, on concentration, decompose and again stain the acid black. No more successful, according to Wispek, seems to be the process of Stolzenwald (*supra*, p. 291).

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[1] *Chem. Zeit.*, 1904, p. 1153.

[2] *Petrol. Rev.*, June 1911, pp. 1045-48.

Pfeifer and Fleischer (Austr. P. 43739 of 1910) treat the acid-tar with silico-compounds; but the yellow acid obtained thus turns black on concentration. The same action takes place when the acid is filtered through bone-charcoal, or when it is heated with nitric acid; and, moreover, their processes are too costly. The widest application has been secured by the process of Hartmann and Benker (continuous concentration in lead pans up to 142° Tw., and then in cascades of porcelain dishes to 168° Tw.), *supra*, p. 104, but this proceeding, according to Wispek, is very troublesome; there is much SO_2 given off, and so much carbonaceous and asphalt-like substance is secreted that the overflows are stopped up, and have to be constantly made free by perforating these crusts, and the concentrated acid is also black. But by the process of the Steaua Romana Petroleum Co. (Austr. P. 42293 of 1910; Ger. Ps. 221615 and 224566; patented in the U.S. America by Blacher and Sztencel, *cf.* p. 292), 75 to 80 per cent. of the sulphuric acid originally employed is recovered in the form of pure white acid of 97 to 98 per cent. The said Company at Campina (Rumania) work up 150 cisterns of crude petroleum at 10 tons each, and produce their own sulphuric and fuming acid by the Tentelew contact process, which yields every day more than a truck-load of acid-tar. In 1907 they introduced the new process, consisting in heating strong pure sulphuric acid in a retort to boiling, and continuously running in black acid, either as such, or as it is obtained from acid-tar by dilution, at the same time passing through the acid a current of air. The supply of black acid is regulated in such manner that the temperature in the retort always remains constant. The vapours formed are cooled in receivers, and yield pure sulphuric acid, which, in case of need, can be subsequently concentrated. The process goes on continuously, and only for the first start fresh pure acid is required. In actual practice 100 vols. of the liquid acid-tar from refining benzene and petroleum is mixed with 50 vols. water in a mechanical agitator, producing 20 to 25 vols. of oily matter and 125 to 130 vols. dilute sulphuric acid 65 to 77° Tw. The oils are washed with water two or three times, and then used as fuel for distilling and concentrating the dilute pure acid; the acid washings are employed for diluting fresh waste acid. The dilute brown acid, separated from the oils, is first boiled down in lead pans to 142° Tw. by means of waste fire-gases, and then run into a retort, the bottom of which consists of a cast-iron dish; the upper part being constructed of acid-resisting fireproof stones, preferably volvic lava. The retorts have a capacity up to 8 cub. metres. They are charged with pure concentrated sulphuric acid, which is heated above 300° (that temperature is required for completely decomposing the organic matter); a current of air is passed through by means of a pipe dipping into the acid. Pure acid of 142° Tw. distils over; the air going away contains much CO_2, but only traces of SO_2. Care must be taken to keep the quantity of the dirty acid in feeding the retort equal to that of the distilling acid, so that the state of concentration within the retort remains always the same. The concentration of the acid distilling over takes place in a similar retort up to 97 to 98 per cent.; the acid of 77° Tw. over here is evaporated together with the 142° Tw. The 20 to 25 per cent. oily matter, produced as stated above, is sufficient for yielding the heat for all the distilling and concentrating operations. The process goes on day and night. The working-up of a truck-load of waste acid per day requires three men at day and two men at night, with a foreman who must be an expert in lead-burning. Such a plant has been continuously at work at Campina since 1908, and other two plants, for a truck-load per diem each, will be started in Galicia. This process of Messrs Blacher and Sztencel must be acknowledged to have completely solved the difficult task of dealing with that troublesome waste product.

E. B. Gray (U.S. P. 1005425) concentrates weak acid derived from petroleum sludge by a series of intercommunicating open pans, followed by a series of stills, also intercommunicating, each provided with a water-jacketed head and condenser. The stills and pans are all placed in the same level on the furnace, the liquid from the last pan discharging into the first still.

Gellen (U.S. P. 1062025) runs the waste acid from refining oils continuously into a decomposing-vessel, placed in an outer vessel heated by a steam-coil. The decomposing liquid is also run into the inner vessel; the mixture formed there runs into he outer vessel, and from this into a settling-chamber provided with a heating-coil, from which the recovered acid and the hydrocarbon oils run off continuously at different heights.

Braünlich[1] (B. P. 2695 of 1913; Ger. P. 267873) runs the acid-tar slowly into fused anhydrous alkaline hydrosulphate, preferably kept in motion, at a temperature above the boiling-point of sulphuric acid, in the same proportion as the pure acid distils off. The presence of a catalyser, *e.g.* cupric sulphate, ncreases the action. Dilute acid may be treated directly by this process.

Kroupa (Austr. P. 67116) regenerates acid from acid-tar by running this in a finely divided state over heated fireproof and acid-proof materials, with admixture of air.

Coster van Voorhut[2] (B. P. 12363 of 1915; Ger. P. 292728) places waste acid from petroleum factories, after dilution with water to about 115° Tw., in a lead-lined, steam-jacketed autoclave, and forces in carbon dioxide until the pressure reaches 7 atm. Steam is then passed through the jacket until the pressure within the autoclave has risen to 10 atm. The heating is maintained for two hours, when the acid will have separated from the tar without any formation of SO_2 or SO_3. The acid and tar are then blown out of the autoclave separately. The CO_2 is washed and used over again.

Bühler[3] (Ger. P. 287555) exposes the waste acid to hot gases, free from oxygen, at a temperature of 273° and upwards, by means of a rotating drum dipping into it. The coke residue left on the drum is removed by a scraper and also recovered.

Still[4] (Ger. P. 29[illegible]775) treats the waste acid in the hot state, in which it is sufficiently thin, with high-pressure steam or with a blasting jet, produced by heated high-pressure gas. The sludge acid thus treated at once separates into pure sulphuric acid and a granular residue, whilst the volatile substances escape together with the steam or gas.

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[1] *J. Soc. Chem. Ind.*, 1913, **32**, 826.

[2] *J. Soc. Chem. Ind.*, 1916, **35**, 528.

[3] *J. Soc. Chem. Ind.* (*Abstr.*), 1916, **35**, 176.

[4] *J. Soc. Chem. Ind.* (*Abstr.*), 1916, **35**, 829.

The Sprengstoff A. G. Carbonit[1] (B. P. 11854 of 1913) avoids the separation of solid substances in heating acid tar, which obstruct the condensing-pipes, by passing the gases and vapours over a surface of water or dilute nitric acid, whereby the organic substances are solidified and deposited at the bottom of the water-vessel, whilst the water is gradually saturated with nitric acid.

C. L. Robinson (U.S. P. 1014520, assigned to the Standard Oil Co.) heats the acid sludge in a still to above 500° F. (260° C.), whereby it is decomposed and a mixture of SO_2 and hydrocarbon vapours is given off. This is passed through a condenser, where the less volatile hydrocarbons are separated, and the gaseous portion is then passed through a sulphur burner and forward to a sulphuric acid plant.

Van Tienen[2] (B. P. 23368 of 1910) adds water and heats the mixture to 140 to 165° under pressure of 7 atm., for a quarter to two hours, according to the nature of the tar. The product separates into three layers, consisting of oil, H_2SO_4, and tarry residues, which can be separated readily. The water added must be sufficient to dilute the remaining acid to a density of not more than 112 to 113° Tw.

Hausman[3] states that the acids recovered in the refining of mineral oil contain about 2 per cent. of sulphonic acids.

Blowski[4] (U.S. P. 1186373 of 1916) dilutes with water, to separate out the tarry matter, and distils rapidly to minimise reduction of the sulphuric acid by organic matter.

Slater[5] (U.S. P. 1263950 of 23rd April 1918) concentrates the sludge acid from mineral oil refining by diluting the sludge with weak acid, separating off, and causing it to flow against a counter-current of heated air which has been blown through a body of previously concentrated acid, in order to concentrate it further and to oxidise impurities therein. The air is finally scrubbed with water to furnish the dilute acid for the initial treatment of the sludge.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1913, **32**, 1130.

[2] *J. Soc. Chem. Ind.*, 1911, **30**, 409.

[3] *Petrol. Rev.*, 1911, **62**, 301 ; *J. Soc. Chem. Ind.* (*Abstr.*), 1911, **30**, 1149.

[4] *J. Soc. Chem. Ind.* (*Abstr.*), 1916, **35**, 839.

[5] *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 363.

Grayson[1] (B. P. 132387 of 31st October 1918) heats the acid recovered from the refining of hydrocarbon oils, with 5 to 10 per cent. pitch from coal-tar or producer gas at 170 to 240° C.

Turner and Davidson[2] (B. P. 131512 of 1st November 1918) describe a similar process.

About 90 per cent. of the sulphur in the waste acids from lubricating oil refining may be recovered in the form of sulphur dioxide, by heating the waste acid; a lower temperature is required for the decomposition, less pitch is formed, and the sulphur dioxide contains less sulphur trioxide when the waste acid from the lubricating oil refining is mixed before heating, with waste from petroleum (burning) oil refining.[3]

Purity of Acid recovered from Tar-Sludge

Schultz[4] describes a refining test for ascertaining the suitability of a sample of sulphuric acid for refining crude petroleum. An addition of 1 c.c. of the acid is made to 100 g. of well-refined petroleum oil in a 150 c.c. flask, which is then closed and shaken vigorously for fifteen minutes. After standing for an hour, the oil is decanted into another flask, shaken with about 2 g. of dry calcium hydroxide, and filtered, and the filtrate compared colorimetrically with the same oil before treatment. The difference in colour may be expressed numerically, by matching it with 98 to 99 c.c. of water, into which a 0·1 per cent. solution of potassium chromate is introduced drop by drop. From 0·3 to 2·5 c.c. (equal to 0·0003 to 0·0025 per cent. K_2CrO_4) are required usually. Of the usual impurities in commercial sulphuric acid, nitrogen oxides, and selenious acid have a strong discolouring influence upon petroleum oil; but no such effect could be observed with sodium sulphate, ammonium sulphate, lead sulphate, arsenic pentoxide, (0·1 per cent.) and hydrochloric acid; whilst the influence of ferric sulphate was doubtful. The discoloration caused by nitrogen oxides is due to partial nitration; whilst the selenious oxide effects oxidation. Commercial sulphuric acid, which had caused discoloration in the refinery, was found to contain from 0·02 to 0·04 per cent. of oxides of nitrogen. In the case of acid containing selenium, the yellow discoloration of the petroleum oil increases with the quantity of acid used for the refining, but when an acid contains only slight traces of oxides of nitrogen, the colour of the petroleum oil may be improved by increasing the proportion of acid, or by using acid of higher concentration.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1919, p. 817.

[2] *J. Soc. Chem. Ind.* (*Abstr.*), 1919, p. 764.

[3] Kolbe, *Petrol. Rev.*, 1919, **14**, 837-847; *Chem. Zentr.*, 1919; [IV], **90**, 197; *J. Soc. Chem. Ind.* (*Abstr.*), 1920, p. 438.

[4] *Chem. Rev. Fett-Ind.*, 1913, **20**, 82-84; *J. Soc. Chem. Ind.*, 1913, p. 409.

Selenium is determined by stirring 10 g. of the acid with 90 c.c. of water, and filtering the separated lead sulphate from the cooled mixture. The filtrate is then treated with 10 c.c. of strong hydrochloric acid and 6 g. of sodium sulphate and heated for a few hours on a water-bath. The selenium, which separates quantitatively as a red precipitate, is collected in a Gooch crucible, washed with water, and dried at 105° C. and weighed.

Nitrous acid is detected best by Ilosvay's reagent, which is prepared by dissolving 0·1 g. of *a*-naphthylamine in 100 c.c. of boiling water; adding 5 c.c. of glacial acetic acid and a solution of 1 g. of sulphanilic acid in 100 c.c. of water, together with a little zinc dust, shaking the mixture, and filtering it rapidly into a flask, which is kept well closed.

For colorimetric determinations, 2 g. of sodium nitrite (about 90 per cent. $NaNO_2$) are dissolved in 100 c.c. of water. and 1 c.c. of the solution added to 99 g. of pure sulphuric acid. The acid will contain then 0·01 per cent. of N_2O_3, and will keep unchanged for a long time. The comparison is made by adding 5 g. of solid sodium acetate to each of two portions of 40 c.c. of water, then 1 c.c. of the reagent, and 1 c.c. of the acid under examination to the first flask, and 1 c.c. of the standard acid to the second flask. The contents must be kept at the same temperature, and the colourations compared after thirty minutes.

Description of a Sludge-Acid Recovery Plant.

Hechenbleikner and the Chemical Construction Co., Charlotte, N.C.[1] (U.S. Ps. 1195075, 1264509, and 1264182), describe an apparatus for the purpose of concentrating sludge acid to at least 168° Tw., and at the same time separating the sludge from the acid. This is accomplished in two stages. The first stage of concentration carries the acid to from 130° Tw. to 145° Tw. At this strength and at the proper regulated temperature, the principal sludge separation takes place. The second stage of concentration carries the acid to 168° Tw.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 414.

First Stage.—The weak sludge acid, following the dilution and separation of the original product, is elevated to a distributing tank located on the top of the preheating tower. Connected to this preheating tower is a flue constructed so as to accommodate a bath of acid. Entering this flue are numerous acid-proof pipes that extend several inches below the surface of the acid. Hot air is furnished through a main header and is distributed through branch headers to the acid-proof iron pipes. The hot air is from 600 to 650°, and is maintained at sufficient pressure only to allow it to ooze through the acid at a pressure of about 2 in. of water. The air entering this acid bubbles through it and drives off the water, leaving the stronger acid together with the sludge, both of which are drained off continuously. In the preheating tower this sludge acid is preheated by the exit gases in order to utilise as much of the heat as possible. The gases leave this tower at a low temperature. In some cases a scrubbing tower is erected for the purpose of removing any organic compound. This is often unnecessary, and depends somewhat on the local conditions and the nature of the sludge. The partly concentrated acid, together with some sludge, is gradually drawn off through an outlet into coolers. From the coolers it enters large tanks provided for intermediate storage in which the principal separation of the sludge from the acid takes place. The sludge is raked off into refuse carts or troughs as needed. No sulphuric acid at all is lost, and some of the hydrocarbons are driven off. Ample tank room is provided, as each day's run is allowed to stand a day or two in order to accomplish full separation.

At the foot of the preheating tower a flue, as above mentioned, is provided with clean-out openings, in order to clean out any sludge that settles and does not come out with the acid. A steam or air jet is provided at the exit-flue in order to create suction when the clean-out openings are uncovered. During the natural process of concentration only natural draught is provided. As above mentioned, weak sludge acid is fed in this apparatus through a distributing tank, and is concentrated in this first stage to from 130° Tw. to 145° Tw. The strength of concentration depends somewhat on the tvpe and nature of the sludge, as the separation takes place at slightly various strengtks, according to the kind of sludge used.

Second Stage.—The second stage apparatus is similar to the first. After the acid has been allowed to stand in separating tanks a long enough period to accomplish satisfactory separation, it is drawn off and elevated to a distributing tank located on the top of a preheating tower. To this preheating tower is also connected a flue, which is so constructed as to accommodate a bath of acid. The acid as it enters the preheating tower is from 130° Tw. to 145° Tw. Further and final concentration takes place in this unit, which is almost identical to the first stage unit. Ordinarily the acid is concentrated to 168° Tw. but as high as 95 per cent. has been accomplished. The gases leave the preheating tower at about 70° C., and of course carry sulphuric acid fumes. For this reason a scrubbing tower is provided for the purpose of reclaiming the acid from the fumes. The gases leave the preheating tower at the top and enter the scrubbing tower at the bottom. The scrubbing tower is packed with spiral rings to provide intensified mixing and scrubbing. The gases leave the tower free from sulphuric acid contents, and enter the atmosphere through an exit stack. Clean-out openings are provided also in this unit, as in the first stage unit, together with coolers and strong acid intermediate storage.

General.—The construction of this apparatus consists principally of lead-lined wooden tanks and acid-proof masonry flues and preheating towers, together with lead scrubbing towers, lead-lined distributing tanks, etc. The first stage and second stage units are very similar in construction and consist principally of a brick-lined lead basin, elevated off the ground on concrete foundations. At one end of this basin a brick tower of sufficient size and height is provided for preheating, and, connected to this tower, covering the balance of the basin, is a brick flue, through which the acid-proof hot-air supply pipes enter. Ample provisions are made for cleaning and regulating the apparatus during operation. Hot air is provided, preferably by the combustion of oil, which takes place in a specially designed combustion furnace, under pressure. This furnace is fed with air and fuel oil sufficient for complete combustion, and also with sufficient surplus air for heating purposes.

With the above-mentioned process, hot gases on entering the liquid below the liquid level, give a sudden cooling, and in such a manner as to prevent dissociation taking place. The concentration takes place below the boiling-point of the acid. This plant is so constructed as to provide continuous operation. The fuel consumption is very economical, as practically the entire quantity of heat units are used in the evaporation of the water. Very little settlement takes place in the concentrating flue, as the majority takes place in the settling tanks provided for the separation. Strong acid, intermediate storage, together with all tanks, coolers, distributing tanks, pans, etc., are constructed in such a manner as to provide for the settling of any sludge, and quick cleaning during operation.

Hechenbleikner and Gilchrist and the Chemical Construction Co., of Charlotte, N.C.[1] (U.S. P. 1310078 of 15th July 1919), describe a furnace for the fractional distillation of sludge acid in a continuous process. The furnace consists of an outer casing of acid-resisting masonry, provided with a grate and an ashpit. Through the top of this casing a cylinder of acid and heat-resisting material projects into the body of the furnace, dividing the latter into two zones, each of which has a separate gas outlet. The top of this cylinder is closed with a bell hopper, through which coal may be fed as required, and is provided with a number of drip-pipes for introducing the sludge acid. When coal is supplied to the furnace in sufficient quantity to maintain the upper level of the fuel bed within the cylinder, as shown in the illustration (Fig. 132), a high-temperature zone is obtained in the lower fuel bed, and a lower temperature zone with the cylinder. The aqueous and tarry constituents of the sludge acid distil off during the passage of the acid through the low-temperature zone, and pass to the tar condenser. The sulphuric acid vapours liberated in the high-temperature zone are collected in a separate condenser. Each condenser is provided with an exhaust fan for the removal of waste gases.

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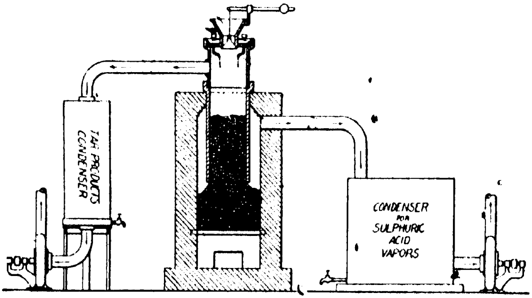
[1] *Chem. and Met. Eng.*, 15th August 1919 p. 211.

Baskerville[1] describes the utilisation of asphaltic base acid sludge obtained in the refining of petroleum and shale oils. The acid sludge is heated by means of live steam, with concentrated sulphuric acid to separate any refinable oil retained by the pasty mass. Three layers form. The oil separating out on top of the mixture is drawn off, and the excess sulphuric acid accumulates at the bottom. The middle portion, which has not been heated high enough and long enough in contact with the strong sulphuric acid to become carbonised and have its asphaltic nature destroyed (as is usually done), is a pasty mass, quite liquid, at the temperature attained, and contains 15 to 25 per cent. of sulphuric acid. It is drawn off and washed once with water, and the asphaltic mass is run at once into a suitable mill and thoroughly mixed with a slight excess of lime (U.S. P. 1234985 of July 1917). The whole mass exhibits the properties associated with asphalt, modified, of course, by the calcium salt present. It becomes fluid when heated sufficiently, and may be applied to metal, masonry, wood, etc. The asphaltic or bitumenic material present may be extracted readily by solvents generally used for dissolving those substances.



FURNACE FOR CONTINUOUS DISTILLATION OF SLUDGE ACID

FIG. 132.

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[1] *J. Ind. Eng. Chem.*, 1920, p. 30; *J. Soc. Chem. Ind.* (*Abstr.*), 1920, p. 182.

The Vitreosil Plant for the Recovery of Sludge Acid.

"Vitreosil" basins have been adopted for the recovery of sludge acid from mineral oil refining, but the shape of the basins has been modified to counteract the tendency to frothing of the acid, as shown in Fig. 133.

The sludge is diluted in lead tanks to about 64° Tw., and then heated by means of lead steam coils fitted inside the tanks, until the acid has been evaporated to about 77° Tw. At this point a considerable amount of the tar separates out, and is skimmed off. The remaining acid is then run into underheat lead pans, and concentrated to 138° Tw. Tar continues to separate in these pans, and is skimmed off as it rises. The acid is now of a dark colour, but is free from tar. It is run directly into the "vitreosil" basin plant, and is concentrated to 168° Tw. For the recovery of 5 tons of 168° Tw. acid per day of twenty-four hours, two steaming pans are required, each 5 ft. by 5 ft. by 3 ft. 6 in. These pans are worked in series, so that the process is continuous. The pans are made of 10-lb. lead, and are fairly durable. The under-fired lead pans are made of 12-lb. and 14-lb. lead, the heaviest pan being nearest the furnace. For the amount of acid mentioned above, two pans are necessary, each 8 ft. by 4 ft. by 9 in. Considerable fuel is saved by mounting these pans directly after the basin plant, and heating them with the waste gases from the concentrator.

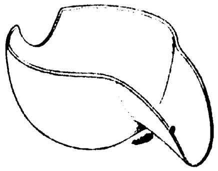

FIG. 133.

Other patents for this object are: Zdaska (Ger. P. appl. Z, 8310); P. and F. M. Murphy (U.S. P. 1094861); Kützer. (B. P. 27977 of 1913).

Recovery of Waste Acid from Benzol Manufacture.

The recovery of waste acid from the manufacture of benzol has also been described.

Gasser[1] (Ger. P. 272130) purifies the waste acid from the manufacture of benzol by forcing through it finely divided hot air. For this purpose the air previously employed for cooling the coke-oven brickwork may be employed, after being finely divided. By this process the impurities collect into lumps, and may be scummed off from the surface. The air is preferably first dried by quicklime; the calcium hydrate formed can be employed for the recovery of the by-products in the manufacture of ammonia.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1914, 33, 587.

The Phœnix A. G., Gelsenkirchen[1] (Ger. Ps. 289162 and 289524) mix the waste acid from the benzol manufacture with ammonia water and with benzol wash-oil, tar-oil, or coal-tar, in order to obtain a concentrated solution of ammonium sulphate and an acid-free tar product by one operation. Or they add ammonia water, containing some chloride, to the mixture of waste acid and tar-oil, and pass steam through the mixture. Owing to the reactions which occur, the temperature rises considerably, and the benzene and its homologues and hydrochloric acid are distilled off and collected.

Stephenson[2] (B. P. 152054 of 2nd May 1919) heats the acid sludge produced in the purification of benzol in a wide shallow pan, by steam introduced through a perforated lead pipe at the bottom of the pan.

Brooke[3] (B. P. 120951 of 18th November 1917) concentrates the waste acid liquors from the manufacture of explosives, such as picric acid, etc., in a series of earthenware or vitreous enamelled vessels, which are heated by steam circulating through coils or the jacketed walls of the vessels, or both. The concentrated acid overflows through a pipe into the next vessel or into a trough.

British Dyes, Ltd., J. Turner, and H. Dean[4] (B. P. 127039) treat the acid liquors from the manufacture of explosives, such as picric acid, etc., with scrap iron or iron filings, until neutralisation and reduction are practically complete.

Recovery of Waste Acids from the Manufacture of Explosives and Nitration Processes.

(*Nitrocellulose, Nitroglycerine, T.N.T., Picric Acid, etc.*)

The spent acids from the various nitration processes are subjected to a denitration process (see Vol. VI.), which varies with the nature of the material from the manufacture of which they result, but consists essentially in the removal of the nitrogen acids leaving a sulphuric acid of suitable composition for concentration. In the case of acids from the manufacture of nitroglycerine and T.N.T., the sulphuric acid from the denitrators contains from 68 to 70 per cent. H_2SO_4, and is run direct to the concentrating plant.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1916, **35**, 422.

[2] *J. Soc. Chem. Ind.* (*Abstr.*), 1920, p. 777.

[3] *J. Soc. Chem. Ind.* (*Abstr.*), 1919, p. 92.

[4] *J. Soc. Chem. Ind.* (*Abstr.*), 1919, p. 555.

Hartmann[1] concentrates waste acid from nitrating processes up to 147° Tw. (sp. gr. 1·732) in six lead pans. The acid, at a temperature of 145° or 150°, then passes through a small "preliminary" cast-iron pan provided with a leaden hood and a chimney for carrying away the vapours, which contain very little acid. Now 180° hot, and of sp. gr. 1·785 to 1·796, it runs into two cast-iron pans with cast-iron covers, one placed higher than the other, and runs away at a strength of 97 to 98 per cent. H_2SO_4. Each of the latter has its own fire, as well as the "preliminary" pan, the waste heat of all heating the lead pans. For the production of 5½ to 6 tons of strong acid in twenty-four hours, the preliminary pan weighs about 24 cwt., the two covered pans with appurtenances, about 7½ tons. The consumption of coal is 20 per cent. The small pan lasts three or four months; the upper one of the large pans six to nine months; the lower one twelve months or more. The castings should be made of hard metal and without flaws, and the two large pans must be entirely surrounded by the fire.

Benker has applied his porcelain apparatus also to the recovery of waste acids. In the case of acid-tar from refining petroleum there is a loss of about 40 per cent.; the acid is coloured black, owing to the formation of graphite, but furnishes water-white petroleum. The recovered acids from nitroglycerine or nitrocellulose are yellowish, but perfectly fit for being used over again.

The recovery of spent acid from the manufacture of picric acid is carried out in two stages: (1) the residual acid is concentrated in a cascade plant to 127 to 135° Tw., and then allowed to cool, when the dissolved picric acid separates out and is removed; (2) the remaining sulphuric acid is then concentrated to the required strength for use in the nitration process. For the preliminary concentration, the most economical method is in lead pans, with an area of 20 to 25 sq. ft. per ton of 130° Tw. acid produced per twenty-four hours (assuming the feed acid is about 70° Tw., and that the pans are worked

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[1] *Chem. Zeit.*, 1899, p. 147.

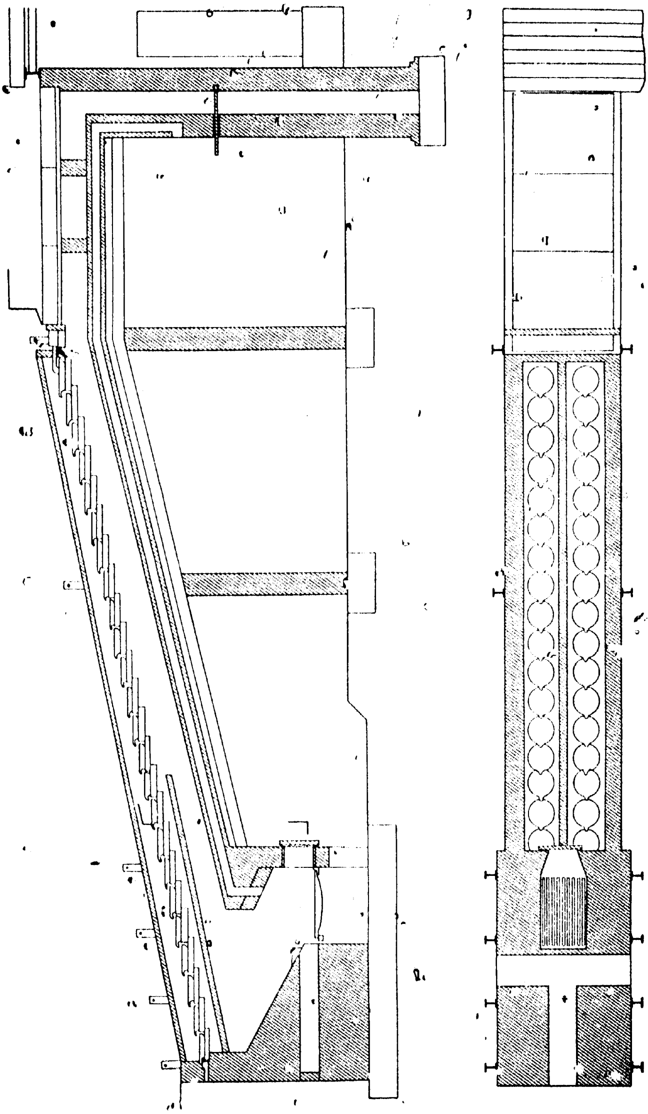

FIG. 134.

continuously with about 9 in. of acid in the pans). The acid is cooled slightly, and then run into lead-lined or stoneware settling-tanks, to deposit the crystals of picric acid. The residual acid from which the picric acid has been crystallised out is then concentrated to the required strength for use again in the nitration process.

The waste acid from the manufacture of T.N.T., etc., is concentrated frequently in a three-stage cascade plant, similar to that described on p. 135. An iron finishing-pan helps to decompose completely the nitro bodies present in the waste acid, and furnishes a high-strength acid, which can be used over again in the nitration processes.

In some plants, instead of denitration by means of steam in a denitrating column, the hot vapours from the iron finishing-pot are drawn through a recuperator tower fed with waste acids. In this way the denitration of the waste acid is effected without much dilution, and hot vapours from the iron pot are condensed partially in the feed acid for the cascade. This plan suffers from the disadvantage that it renders it impossible to control the working of the plant by means of the strength of the distillate from the iron pot (see p. 135).

The condensers for cascade concentrators working on this class of waste acids are packed with an open packing, and worked hot to prevent blockage from the decomposition of dinitro and trinitro bodies. Earthenware towers, packed with rings, give satisfactory results for this purpose, and a steam injector at the condenser inlet not only assists the draught but also helps to keep the condensers hot.

In a private communication to the author, Messrs J. F. Carmichael & Co., Ltd., Tower Building, Liverpool, give particulars of the cascade plants erected for the concentration of waste sulphuric acid from nitration processes at Messrs British Dyes, Ltd., Huddersfield.

Figs. 134 and 135 show the general arrangement and detail of the plant, which consists of two batteries of five cascades each. The waste acid, after settlement, is delivered into supply-tanks on the ground floor, whence it is elevated to the large feed-tanks on the upper platform. From here it flows by gravitation into the three preheating lead pans, and thence into the main concentrating chamber, consisting of twenty-four stepped basins fitted with special deflectors (see p. 129). The concentrated acid is received into coolers at the foot of the cascade, from which it flows into the strong-acid storage-tanks. Each cascade produces 5 tons of 95 per cent. sulphuric acid per twenty-four hours, when fed with acid of 80° Tw. from the manufacture of picric acid, or nitro, dinitro, trinitro, benzene, or toluene.

The fuel used at first was coal or coke in an ordinary fire grate, but the system has since been converted into gas firing.

The condensation of the acid vapours is effected in four stoneware scrubbers, 3 ft. diameter and 9 ft. high, packed with acid-resisting earthenware rings. The acid vapours pass through the condensers in series; and the first two condensers are lead-covered, on account of the heat. From the scrubbers, the gases pass through a final wash-scrubber, and then into the chimney flue. The dilute acid condensed in the scrubbers is collected and returned to the lead preheating pans.

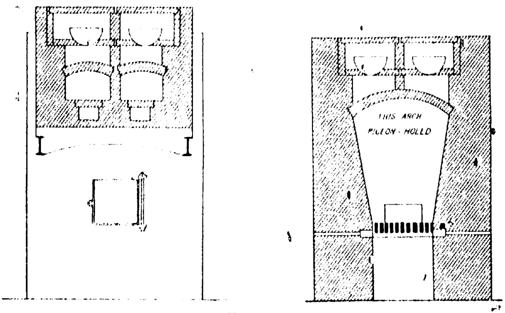

FIG. 135.

According to information supplied privately to the author, the following results were obtained on a typical three-stage cascade plant, consisting of preheaters, basins, and an iron rectifying pot, in series, with tar-firing working on T.N.T. waste acids.

Preheaters.—The preheater consists of pans, 35 in. by 35 in. by 9 in., built of 12-lb. lead, with an acid depth of about 6½ in. Ten pans are connected in series, and each pan is stiffened on three sides with iron, and has a broad overhanging lip communicating with the next lower vessel. The two lowest pans are placed on solid cast-iron seatings. The feed

Basin Losses during a period of 37 weeks.

Basin No.	Unit A.		Unit B.		Unit C.		
22					1	1	Open seatings (10-22)
21							
20						1	
19							
18							
17					1		
16				2		1	
15					1	2	
14			1	1	3		
13		1	1	9	7	5	
12	1	1	5	7	13	4	
11	1	1	8	9	13	8	
10	3	5	21	11	23	16	
9	8	7	9	17	11	12	Solid and semi-solid seatings (4-9)
8		1	10	11	16	9	
7	1		4	11	9	5	
6			5	4	6	1	
5		1		5	5	1	
4	1	1	1	1			
3	1	1	1	2	6	2	Open seatings (1-3)
2	1	1	1		1		
1		1					

To rectifiers. (Unit A)

To rectifiers. (Units B and C)

acid (64 to 66 per cent. H_2SO_4) enters the plant from the denitrators at a temperature of 70 to 90° C., and leaves the preheaters at a temperature of 150 to 160° C. and a strength of 70 to 76 per cent. H_2SO_4. The life of the upper pans is reduced by the presence of nitrogen acids in the feed acid; but the lower pans receive the greatest wear and tear, due to excessive heat. Cast-iron pans were tried in the lowest positions, but were attacked rapidly.

Basins.—There are two parallel rows of twenty-two double-lipped narki basins, of approximately 2-gall. capacity. Although unaffected chemically by the acid, they crack frequently, as shown in the table on page 309.

Sludge acid is deposited from position 12 downwards, and the basins are cleaned out at least once in twenty-four hours. The acid leaves the basins and enters the rectifier at a strength of 90 to 91 per cent. H_2SO_4.

Rectifiers.—The cast-iron rectifiers are of standard design, and are worked with a depth of 6 in. of acid. The acid is heated to a temperature of 280 to 300° C., and leaves at a strength of 93 to 94 per cent. H_2SO_4.

The pans are sludged out at least twice per week, but holed frequently at the sides and ends above the level of the sludge deposits. One pan was very thin at the acid level, but, in other cases, pitting had occurred below this level, due probably to lack of homogeneity in structure.

The plant is fired with tar fuel (consisting of 60 per cent. pitch and 40 per cent. creosote oil) in a wrought-iron burner (tar aperture $\frac{1}{16}$ to $\frac{3}{32}$ in., surrounded by a steam jet); and a temperature of 1100 to 1200° C. is obtained in the combustion chamber. The average weekly output per unit is about 50 tons of 94 per cent. H_2SO_4, with a fuel consumption of 0·16 to 0·2 ton of tar per ton of concentrated acid. The output is lower with gas-firing, and an average fuel figure is about 0·25 ton per ton of finished acid, to which must be added the steam used in the producer—say, 10 per cent., making 0·275 ton in all.

The following figures on the concentration of waste acids from the manufacture of T.N.T. and nitrocellulose are abstracted from the Report on the Statistical Work of the Factories Branch of the Department of Explosives Supply, Ministry of Munitions (pp. 129 and 145):—

H.M. FACTORY, QUEEN'S FERRY.
Monthly Report. Month ending 6 A.M., 29th December 1917.

N.C. CASCADES.

Sulphuric Acid Concentrators (N.C.).

Units Working, 2·7.

CHARGED.	Tons.	Per cent. H_2SO_4.	Tons H_2SO_4.	Tons SO_3.	PRODUCED.	Tons.	Per cent. H_2SO_4.	Tons H_2SO_4.	Tons SO_3.
Sulphuric acid	212·4	67·33	143·0	116·5	Sulphuric acid . (strong)	140·1	89·65	125·6	102·6
Fuel—					Sulphuric acid . (weak)	...	...	...	
Coal used .	35·8				Total .	...	...	...	

LOST.

Sulphuric acid—	Tons.	Tons SO_3.
Total H_2SO_4 charged to plant	143·0	116·5
Total H_2SO_4 recovered	125·6	102·6
Amount lost	17·4	13·9

Per cent. lost, 12·2 per cent.

Physical and Working Data.

	Tons.	Temperature °C.	Per cent. of H_2SO_4.	Draught.
Acid charged per unit. . . .	5·9	20	67·33	...
Acid concentrated per unit . . .	3·89	15	89·65	...
Acid from scrubbers	...	33	30·5	...
Gases to scrubbers	...	57	1·1	...
Gases from scrubbers	40	23	1·35	...

	Grains per cub. ft.	Velocity ft. per Scrubber at 15° C.	Tons H_2SO_4 per Unit per 24 hours.	Total H_2SO_4 per 24 hours.
Scrubber exit gases	0·575	...	...	...
Stock exit gases	0·9	...	...	...

Coal used per ton of H_2SO_4 produced	0·285
Coal used per ton of concentrated acid produced (H_2SO_4, 89·65 per cent.) . .	...
Water evaporated per unit per 24 hours	1·7
Total water evaporated per 24 hours	3·5

REMARKS—Plant shut down 17th December, restarted 19th December.
Plant shut down 23rd December, restarted 28th December.

H.M. FACTORY, QUEEN'S FERRY.
Monthly Report.

Month ending 6 A.M., 29th December 1917.

T.N.T. CASCADES.

Sulphuric Acid Concentrators.

Units Working, 3·4.

CHARGED.	Tons.	Per cent. H_2SO_4.	Tons H_2SO_4.	Tons SO_3.	PRODUCED.	Tons.	Per cent. H_2SO_4.	Tons H_2SO_4.	Tons SO_3.
Sulphuric acid	462·0	66·49	307·2	250·6	Sulphuric acid. (strong)	301·0	89·20	268·5	218·9
Coal used .	67·5								

LOST.

	Tons.	Tons SO_3.
Sulphuric acid—		
Total H_2SO_4 charged to plant	307·2	250·6
Total H_2SO_4 recovered	268·5	218·9
Amount Lost	38·7	31·7

Per cent. lost, 12·59 per cent.

Physical and Working Data.

	Tons.	Per cent. H_2SO_4.	
Acid charged per unit	9·05	66·49	
Acid concentrated per unit	5·9	89·20	

Coal used per ton of H_2SO_4 produced	0·251 tons.
Water evaporated per unit per 24 hours	2·3 „
Total water evaporated per 24 hours	7·1 „

REMARKS.—Plant shut down 1st December, 10 A.M., restarted 5 P.M.
Plant shut down 12th December, restarted 14th December.
Plant shut down 17th December for four hours.
Plant shut down 20th December to 29th December.

According to the Second Report on Costs and Efficiencies for H.M. Factories issued by the Department of Explosives Supply, Ministry of Munitions (pp. 59-60), the average efficiency of the Kessler plants at H.M. Factory, Pembrey, was as follows:—

(*a*) *T.N.T. Waste Acids*—

Efficiency	October to December 1917 (13 weeks)	91·3 per cent.
„	January to June 1918 (26 weeks)	93·1

(*b*) *Nitroglycerine and Nitrocellulose Waste Acids*—

Efficiency	July to December 1917 (26 weeks)	93·2 per cent.
„	January to June 1918 (26 weeks)	93·0 „

Recovery of Waste Acid from Metal Works.

Methods for the recovery of sulphuric acid from the waste acids produced in the treatment of metals have been described.

Pughsley (B. P. 1538 of 1864) recovers sulphuric acid from the refuse "pickle" of tin-plate works, by evaporating the solution and separating the crystals of ferrous sulphate. The mother liquor can be used again as a pickle after further concentration.

Madge (B. P. 3217 of 1867) proceeds in a similar manner.

Lavender, Richards, and Williams (B. P. 3182 of 1878) filter, evaporate down, and allow to crystallise. The crystals are heated in fireclay retorts, and the acid vapours led into a chamber plant.

Parker and Robinson (B. P. 10554 of 1889) evaporate the solution to a specific gravity of 1·4 to 1·5 in contact with iron, and add strong sulphuric acid, which precipitates anhydrous ferrous sulphate, which is then distilled.

Parker (B. P. 9632 of 1889) proposes to regenerate the acid by electrolysis, and deposit the iron on the cathode.

Anderson[1] (B. P. 3505 of 1913) mixes the waste acid with an excess of milk of lime, agitates for two or three hours, allows the precipitate (consisting of ferrous hydrate, calcium sulphate, and a little calcium hydrate) to settle down, and pumps it into filter presses. The cakes remaining in these are exposed to the air for a few days, until the ferrous hydrate has changed completely into ferric hydrate, which is used for the purification of gas, or for the preparation of gypsum, according to whether ferric hydroxide or calcium sulphate prevails.

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[1] *J. Soc. Chem. Ind.*, 1914, **88**, 312.

Howl and Perry[1] (B. P. 5830 of 1914) evaporate down the solution to a concentration of about 75 per cent. H_2SO_4, when the dissolved iron separates out in the form of ferrous sulphate.

Natho (Ger. P. 262466) treats sulphuric acid contaminated by inorganic salts without evaporation with equivalent quantities of calcium carbonate and sand, made into a paste, with addition of a little water in an autoclave to 600 to 800° ; pure sulphuric acid or sulphur trioxide distil off, and calcium silicate remains behind.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1915, **34**, 423.

CHAPTER VII

COSTS AND EFFICIENCIES

ONE of the most interesting developments in recent years is the increased attention given to the preparation of accurate cost accounts.

The graphical system of representation instituted by Mr K. B. Quinan, and published in the First and Second Reports on "Costs and Efficiencies," for H.M. Factories controlled by Factories Branch, Department of Explosives, is a striking object lesson of the valuable results which can be achieved in this respect. These statistics were compiled from two points of view: (1) the plant or technical aspect, and (2) the "costing" aspect. In connection with the first, extremely detailed records of plant working were prepared, from which weekly and monthly summaries of efficiencies were made. Side by side with the technical records detailed accounting work was carried on, and it was found that the translation of weights and quantities of losses into terms of money values proved of the greatest assistance in stimulating efforts towards reaching the highest possible efficiency of working.

The following information has been abstracted from the section of the reports dealing with the concentration of sulphuric acid.

In order to show the costs of concentration on a fair comparative basis, costs were reckoned per ton of 100 per cent. sulphuric acid delivered, and the amounts of H_2SO_4 lost per ton of H_2SO_4 delivered were charged uniformly at £7 per ton of H_2SO_4.

The cost of concentration is made up of: (1) raw materials used, *i.e.*, loss of acid, which depends entirely on the efficiency of working; (2) service charges, which include the following items—(*a*) process wages; (*b*) fuel, water, power, etc.; (*c*) plant general expenses; (*d*) maintenance of plant and buildings; (*e*) on cost, a proportion of the general factory expenses allocated on the basis of wages.

A copy of the details of the service charges for June 1918, at H.M. Factory, Gretna, is given below.[1]

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[1] Report on the Statistical Work of the Factories Branch, p. 159.

H.M. FACTORY, GRETNA. Four weeks ending 29th June 1918.

CONCENTRATION PLANT COST.

Service Charges Cost Sheet.

Details.	Quantity.	Rate.	Amount. Detail.	Amount. Total.
PROCESS WAGES:—			£ s. d.	£ s. d.
(*a*) Salaries of plant officers			107 2 3	
(*b*) Operative wages			317 2 5	
(*c*) Overtime allowances			30 6 7	
(*d*) Yard and traffic			42 11 7	
				497 2 10
MAINTENANCE OF PLANT AND PROCESS BUILDINGS:—				
(*a*) Materials			125 10 2	
(*b*) Wages			412 12 11	
(*c*) Oncost (shops and salaries)			236 16 10	
				774 19 11
FUEL, WATER, POWER, etc.:—				
(*a*) Direct fuel, coal				
,, coke				
,, gas, as coal	878·59 tons	£1·9795	1,739 4 10	
,, oil				
(*b*) Water and water power	11,580,148 gls.	1·886d. p. 1000	91 0 1	
(*c*) Electric power and light	30,094 units	0.551d. p.u.	69 2 8	
(*d*) Compressed air			50 12 1	
				1,949 19 8
PLANT GENERAL EXPENSES:—				
(*a*) Plant stores			6 19 0	
(*b*) Clothing			37 15 4	
(*c*) Shift house and mess rooms			13 8 8	
(*d*) Steam for compound			122 4 0	
				180 7 0
ONCOST (factory general expenses)			340 13 0	
				340 13 0
ADJUSTMENT FOR:—				
Scrap *ex* Plant			*8 8 6*	
,, ,,			*178 16 0*	*187 4 6*
				3,555 17 11

FACTORY CHARGES—

	£ s. d.
Normal	247 3 7
Abnormal—township	69 13 7
Abnormal—transport of workers	23 15 10
	£340 13 0

Process Wages.

Under this heading are shown the following sub-headings:—

(a) *Plant officers.*—Salaries of all plant officers, including chemists and engineers whose whole time is spent on the plant.

(b) *Operative wages.*—Wages of foremen and all process workers.

(c) *Overtime allowances.*—The excess wages earned by overtime rates, over and above the ordinary rates, the overtime wages at ordinary rates being shown as "operative wages."

(d) *Yard and traffic.*—The labour cost of handling raw materials and products into and out of the plant.

Maintenance of Plant and Process Buildings.

Under this heading are given all expenses, sub-divided into:—

(a) *Materials.*

(b) *Wages.*

(c) *Oncost* (shops and salaries).—This item includes cost of repairs—shops, salaries of maintenance engineers, foremen, tradesmen, etc.

Fuel, Water, Power.

Under this heading are shown all fuel and other sources of power, grouped, as follows:—

(a) *Process fuel.*—The quantities and sterling amounts of direct fuel consumed, separate headings being shown for coal, coke, gas, and oil.

(b) *Water and water power.*

(c) *Electric power and light.*

(d) *Compressed air.*

Under each of these services is given the proportion of expenditure on such services allocated to the concentration plant, including engineers' salaries, where these can be allocated directly. Expenditure, however, of a direct nature (such as engineers' shop charges), which, while not admitting of specific allocation, refers generally to several of the above headings, is apportioned between and included in the expenditure under such heads.

Plant General Expenses.

This is divided into :—

(a) *Plant stores.*
(b) *Clothing.*
(c) *Shift houses and mess rooms.*

Oncost (General Expenses).

A proportion of the general oncost of the factory (allocated on the basis of operative wages) is charged to the concentration plant cost. The general oncost includes all office, management, and stores charges, and any other overhead expenses which cannot be allocated directly.

Adjustment For.

This heading allows for credits for sales of scrap, etc. For example, frequently in trade factories the weak acid from the scrubbers and condensers is sold as accumulator acid.

It is important to note that no allowance is made in these figures for rent, rates and taxes, insurance, depreciation, or interest on the capital expenditure of the plant, which form an integral portion of the cost of concentration of the average trade factory, and which must be considered carefully when deciding on the best form of concentrating plant to suit the required conditions. It is customary in most trade factories to calculate depreciation on sulphuric acid plant at the rate of 15 per cent. per annum on the written-down value of the plant, as accepted by the Inland Revenue Authorities for taxation purposes. Under this system all additions and repairs to the plant for the year must be added to the capital value before the 15 per cent. allowance for depreciation is obtained.

Interest on the capital expenditure of the plant is based generally at the rate of 5 to 6 per cent. per annum on the same capital value as used for depreciation purposes.

In the process of concentration there is always a certain loss of acid, which varies with the efficiency of the plant working, and the value of the acid lost must be included in the cost of concentration. In the case of the Government Factories, by means of an elaborate system of storage tanks and measurements, the quantity and strength of the feed acid and of the finished acid were recorded accurately. Table A shows the

TABLE A.

H.M. FACTORY, GRETNA. — Four weeks ending 29th June 1918.

Weak Sulphuric Acid Account (as 100 per cent. H_2SO_4).

Date.	Details.	Tons.	Rate.	Amount.			Date.	Details.	Tons.	Rate.	Amount.		
			£	£	s.	d.				£	£	s.	d.
June 1	To stock as per last A/c.	1835·85	5·81	10,666	5	9	June 29	By concentrators	6561·8	5·935	38,943	3	10
" 29	" S.A. *ex* S.A. distribution A/c.	13·56	6·37	86	7	6							
" 29	" Grillo	234·8	5·81	1,364	3	9							
	" stills	5106·2	5·991	30,591	8	5		" charged to system owing to starting up Nos. 5 and 6 towers	14·7	...	87	5	0
	" denitrators	1100·3	5·991	6,591	18	0		" stock	1714·21	5·99[illegible]	10,269	14	7
		8290·71		49,300	3	5			8290·71		49,300	3	5
RECOVERED ACID AT CONCENTRATORS (as 100 per cent. H_2SO_4).													
June 29	To weak acid charged	6561·8	5·935	38,943	3	10	June 29	By loss at concentrators	76·9	...	...		
	" plant expenses	...	...	3,555	17	11		" production of sulphuric acid charged to S.A. distribution A/c.	6484·9	6·567	42,586	6	9
	" weak S.A. charged into system owing to restarting two towers, Nos. 5 and 6, 14·7 tons	...	...	87	5	0							
		6561·8		42,586	6	9			6561·8		42,586	6	9

Average strength of acid charged—77·08 per cent. *Average strength of acid recovered*—93·02 per cent. *Loss in concentration*—1·17 per cent.

weak sulphuric acid balance sheet and also the final cost of concentrated acid for June 1918, at H.M. Factory, Gretna.[1]

Although it should be carried out wherever possible, in the average works it is not always practicable to measure the feed acid to the concentrators in so accurate a manner, and it is therefore necessary to rely on the results of trial runs made at regular intervals. The average efficiency of the concentrating plants during the war period (1914-1918) may be taken approximately as follows:—

Cascade Plants	85 to 90 per cent.
Kessler "	91 " 93 "
Gaillard "	96 " 97 "

The monthly concentration costs are summarised in the form shown in the table[2] on p. 321, by means of which variations from month to month under each heading in the cost per ton can be reviewed readily. A still more elaborate and impressive method is to present the comparative costs in a graphical form, as shown in Fig. 136, which gives the average comparative costs for four six-monthly periods for different types of concentrating plant in use at the various Government factories. The costs for the Gretna Gaillards from January to June 1918 are included in this figure, because they were the lowest cost figures recorded on any concentration plant during the period under review. In spite of the enormous overhead factory charges (welfare, housing, transport, etc.), Gretna combined a remarkably high efficiency with very low service charges.

In considering these comparative figures, it should be borne in mind that the cost of stores and labour increased steadily during the period under review. For example, it is stated that at one factory from 1914 to August 1918 the average weekly wages of labourers increased from 25s. to 55s.; of process workers, from 30s. to 82s.; of tradesmen, from 32s. to 70s.; and of lead burners, from 69s. during January 1916 to 97s. in June 1918; and these figures may be taken as representative of the general increase in wages throughout the whole of the chemical industry.

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[1] Report on the Statistical Work of the Factories Branch, p. 160.

[2] *Ibid.*, p. 36.

COST SHEET [illegible]—SUMMARY OF TOTAL COST.

Concentration.

No.	Plant and Period.	H_2SO_4 Delivered.		Efficiency.	H_2SO_4 Lost at £7 per ton.		Wages.	Fuel.	Water, Steam and Power.	Mainten-ance.	General Expenses.	Total Services.	Total Cost.	Entered.	Checked.
	Gretna.	Tons.	Strength per cent.	Per cent.	Tons.	£	£	£	£	£	£	£	£		
	July 1918	7187·8	...	98·9	76·7	536·9	643·967	1996·45	218·271	965·204	602·300	4426·192	4963·092		
	August	5771·3	...	98·0	119·1	833·7	554·054	1668·875	211·779	846·446	532·538	3813·692	4647·392		
	September	6372·5	...	98·5	100·3	702·1	646·329	2068·113	252·663	1061·992	601·954	4631·051	5333·157		
	October	8955·5	...	98·3	151·6	1061·2	783·492	2800·171	256·492	1523·217	658·604	6021·976	7083·176		
	July-October 1918	28287·1	..	98·4	447·7	3133·9	2627·842	8533·609	939·205	4396·859	2395·396	18892·911	22026·811		

COST SHEET C_2—SUMMARY OF COST PER TON.

Concentration.

No.	Plant and Period.	H_2SO_4 Delivered.		Efficiency.	H_2SO_4 Lost at £7 per ton.		Wages.	Fuel.	Water, Steam and Power.	Mainten-ance.	General Expenses.	Total Services.	Total Cost.	Entered.	Checked.
	Gretna.	Tons.	Strength per cent.	Per cent.	Tons.	£	£	£	£	£	£	£	£		
	January-June 1917	17234·4	...	95·2	0·0518	0·363	0·167	0·364	0·049	0·210	0·122	0·912	1·275		
	July-December 1917	27397·38	...	96·4	0·038	0·264	0·153	0·392	0·058	0·384	0·166	1·148	1·412		
	January-June 1918	31280·2	...	98·7	0·013	0·091	0·098	0·301	0·045	0·120	0·081	0·645	0·736		
	July	7187·8	...	98·9	0·011	0·076	0·089	0·278	0·030	0·134	0·084	0·615	0·690		
	August	5771·3	...	98·0	0·021	0·144	0·096	0·289	0·037	0·146	0·092	0·660	0·804		
	September	6372·5	...	98·5	0·016	0·110	0·101	0·325	0·040	0·167	0·094	0·727	0·837		
	October	8955·5	...	98·3	0·017	0·118	0·087	0·313	0·029	0·170	0·074	0·673	0·791		
	July-October 1918	28287·1	...	98·4	0·016	0·111	0·093	0·30[illegible]	0·033	0·155	0·085	0·668	0·779		

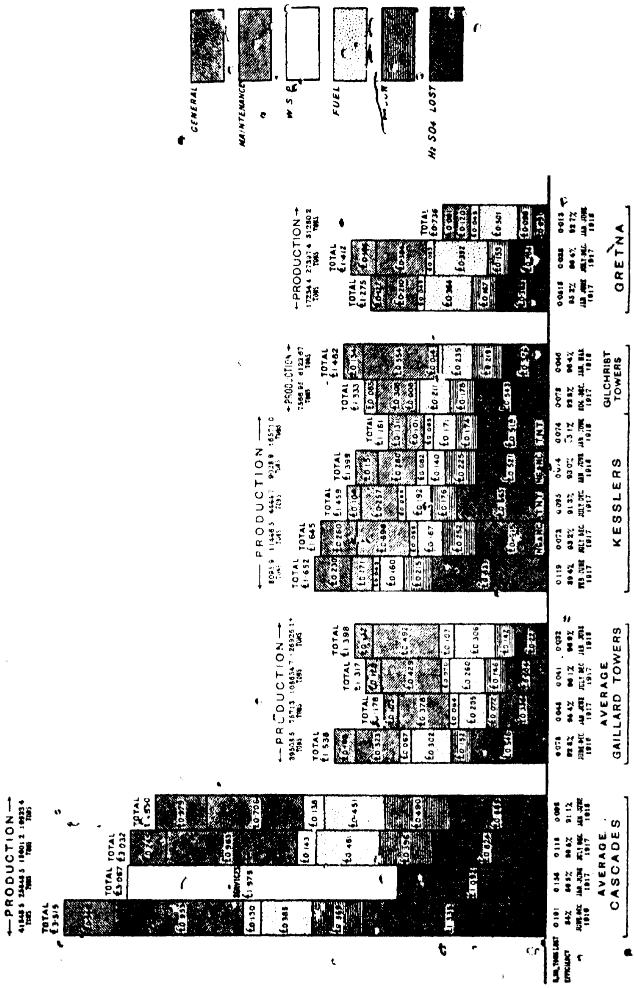
GENERAL
MAINTENANCE
W.S.R.
FUEL
LABOUR
H₂SO₄ LOST
PRODUCTION
TOTAL £3·515
TOTAL £3·067
TOTAL £3·032
TOTAL £1·550
SERVICES £1·975
AVERAGE CASCADES
AVERAGE GAILLARD TOWERS
KESSLERS
GILCHRIST TOWERS
GRETNA
EFFICIENCY

FIG. 136.

The results achieved in the Government factories from June 1916 to June 1918 indicate that from the point of view of plant efficiency, fuel consumption, maintenance, and labour charges, the cascade system of concentration compares very unfavourably with either the Gaillard or Kessler plant, but it must be remembered that the acid concentrated on these plants was the waste acid from the manufacture of explosives containing various impurities. When working on clean chamber acid, much better results can be obtained with the cascade system.

The very excellent results obtained with the Gaillard plant at Gretna indicate that this type of plant is more economical to work in all respects (except fuel consumption) than the Kessler plant when large quantities of sulphuric acid are to be concentrated. Again, it must be remembered, however, that the feed acid for the concentrators was the waste acid from the manufacture of explosives, which contains an appreciable quantity of organic and mineral impurities. With dirty acids the Gaillard plant has the marked advantage that it is practically self-cleaning, and does not require a shut-down for this operation as in the case of the Kessler. When concentrating chamber acid for sale, however, the Kessler plant is much more flexible and convenient than the Gaillard plant, and can be worked more closely to definite and high percentages of concentration. The Kessler apparatus also is less costly to instal in the average works, and it is usually possible to arrange a gravity feed to it; whereas the height of the Gaillard tower renders this quite impossible.

The experience with the Gilchrist concentrator at Queen's Ferry is unfavourable to this type of plant. The efficiency never reached the standard of a good Gaillard tower, and the cost was usually much higher.

Apart from the Government reports quoted above, there is little or no data available on the present-day costs of concentration, except from American data, which emanate almost entirely, however, from trade sources.

According to A. E. Wells and D. F. Fogg,[1] the cost of concentrating acid from 60 to 66° Bé. (142 to 168° Tw.) on a 10-ton cascade plant with 100 dishes 12 in. in diameter and 60 preheating pans 24 in. by 12 in. is as follows:—

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[1] Bulletin 184, U.S. Department of the Interior, p. 137.

Coal 17 per cent. at $5·00 per ton	$0·85
Labour	1·25
General expenses and repairs	1·00
Losses 4 per cent. of acid, assuming 60° Bé. acid at $8·00 per ton	0·30
Operating cost per ton 66° Bé. from 60° Bé.	$3·40

P. S. Gilchrist[1] supplies some interesting information on the comparative costs of concentration in America, and describes various types of tower concentrating plant.

Combinations of cascade and tower systems have been used. An installation at Baltimore in 1916 with twelve iron pans 36 in. in diameter, in two rows, produced 23 tons of 66° Bé. (168° Tw.) acid per twenty-four hours from 54° Bé. (120° Tw.), the acid entering the top pans being 57° Bé. (131° Tw.) at 290° F. (143° C.).

Actual *operating* cost per ton of acid is as follows:—

Fuel oil, 19·5 galls. at 4 cents	$0·78
Labour	0·71
General expenses and repairs	0·85
Losses, 10 per cent. of acid, assuming 60° Bé. acid (142° Tw.) at $8·00 per ton	0·80
Operating cost per ton of 66° from 54° Bé. (120° Tw.)	$3·14

Particulars are given also of a plant in which concentration is accomplished: (1) by surface evaporation in a pan flue; (2) by tower evaporation and preheating.[2]

Two 50-ton units of this type of concentrator have been installed for the Standard Oil Co., and recent figures show that, during a period of a little more than four years, over 140,000 tons of acid of 66° Bé. (168° Tw.) acid has been turned out with a repair and upkeep cost of less than $10,000. This works out at 7 cents to 8 cents per ton of finished acid. The oil consumption was from 10 to 11 galls. per ton of 66° (168° Tw.) acid, starting from 55° Bé. (123° Tw.). One man per shift operates the entire plant, and the cost of operation is as follows:—

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[1] *Chem. and Met. Eng.*, 21st June 1922, 26, No. 25.

[2] *Cf.* Gilchrist concentrator, p. 239.

Fuel, 11 galls. at 4 cents	$0·44
Labour	0·12
General expenses and repairs	0·30
Losses 3½ per cent. based on $8 per ton of 60° (142° Tw.) acid	0·28
Operating cost per ton of 66° acid from 54° Bé. (120° Tw.)	$1·14

Gilchrist describes also a further modification of this system, which is called a hot-air submergence type of plant. It is designed to concentrate any kind of sulphuric acid, but especially separated sludge acid of any quality. The underlying principle of the process is concentration by blowing hot air at a temperature of about 1200° F. (650° C.) through the acid. *Cf.* pp. 299-301.

Figures are given showing the comparative cost of concentrating sludge acid by the old and new method.

(1) Cost of producing 66° (168° Tw.) acid from 35° Bé. (65° Tw.) sludge acid, using lead pans and cast-iron stills:—

100 galls. oil at 4 cents	$4·00
Labour	0·60
General expenses and repairs	2·50
Losses 20 per cent. based on $8 per ton of 60° (142° Tw.) acid	1.60
Operating cost per ton 66° (168° Tw.) from 35° (65° Tw.) acid	$8·70

(2) Cost of producing 66° (168° Tw.) from 35° Bé. (65° Tw.) sludge acid, using the hot-air submergence plant:—

35 galls. oil at 4 cents	$1·40
Labour	0·20
General expenses	1·10
Losses 6 per cent. based on $8 per ton 60°	0·48
Royalty	1·00
Operating cost per ton 66° (168° Tw.) acid from 35° (65° Tw.)	$4·18

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CHAPTER IX

THE TRANSPORT OF SULPHURIC ACID

Carboys

SULPHURIC acid was formerly always, and is even now to a great extent, sent out in carboys (from the Persian, *qarabah*), a large and more or less globular glass bottle, with a neck long enough to pour the acid clear of the packing and container. The British Railway Companies in their 'General Classification of Goods, give the following definition :—

"The term 'carboy,' as used in this classification, means a globular bottle of not more than 12 galls. capacity, made of glass not less than ⅛ in. thick in any part, practically free from striæ and bubbles, carefully annealed, and with the initials of the maker, or other distinguishing mark, on the neck."

"For liquids not exceeding 1·2 sp. gr. carboys up to 14 galls. capacity may be used."

The above specification, however, has not been found possible of attainment, since no bottle maker would guarantee the thickness. In Great Britain glass carboys are made chiefly in Lancashire and Yorkshire, and the process of manufacture, as well as the finished carboy, is practically what it always has been from very ancient times. The heated glass is "gathered" on the end of an iron pipe from the melted mass in the furnace, and after skilful manipulation of the mass, the workman blows it up with his mouth, like a rubber toy balloon, till it has the requisite capacity, judging the capacity entirely by the eye, only the lower part being formed in a mould. A rough collar of glass is wrapped round the neck, and when the whole is sufficiently cooled, the blowpipe is broken off close to the collar, and after annealing (gradually and slowly cooling) the carboy is finished, the mouths being from 2 in. to 2½ in. diameter, though somewhat rough and irregular (Fig. 137).

In other European countries, the carboys are made in a similar way, but with mouths only from 1 in. to 2 in. diameter; the mouths are generally better finished, but the larger diameter of the British carboy is preferable for pouring, because air can get into the carboy above the heavy flowing liquid, and there is not the same tendency to splash.

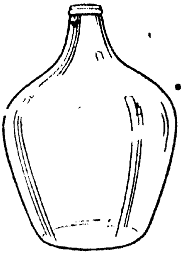

FIG. 137.

In America, carboys of cylindrical form, instead of globular, are now being machine-made, with well-finished mouths, but they are about double the weight of the hand-made British carboys. Attempts were made many years ago to produce square carboys, in order to economise space, but the difficulties of unequal contraction in cooling, and consequent cracking, could not be overcome.

In Great Britain and America the usual or standard capacity of a carboy is 10 galls., any other capacity being special; but in most other European countries, and Germany in particular, 60 to 65 litres (about 13 galls.) is the usual size.

Sometimes glazed earthenware vessels of various capacities are used, especially in France and Bohemia.

Stoppers for Carboys.

For pure acids, it is usual to employ glass carboys with ground-in glass stoppers, but these are much too costly for the ordinary trade. The ordinary stopper is of glazed earthenware, but more often of common brick, round and about which is pressed a lump of soft moist clay with a cloth tied over it to keep it in position. Sometimes stoppers are first luted with plaster of Paris, and with a mixture of ground barytes and coal-tar pitch.

Hampers for Carboys.

It is obvious that a glass vessel, containing from 150 to 180 lb. of sulphuric acid requires protection from breakage, and some means of handling it. In former years, a rough wickerwork basket was universally used for this purpose, the space between the glass and the basketwork being tightly rammed with straw packing up to the shoulders (the largest diameter) of the carboy; but sometimes twisted straw bands are continued to the top of the neck, for better protection of the glass, especially when stowed in tiers. The wicker baskets were very unsatisfactory and unsafe for the weight they had to carry. Owing to the presence of acid in the straw or on the floor, the bottom frequently dropped out, while the handles and upper parts broke away, especially in dry weather. They seldom were fit for more than one journey. An innovation was made by Richard Leigh (B. P. 3991 of 1876) (Figs. 138 and 139) of a carboy hamper made from fluted hoop iron, protected by a thick coating of coal-tar, in which the usual straw packing is used, as with the wicker basket.

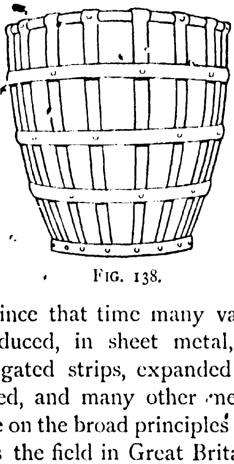
FIG. 138.

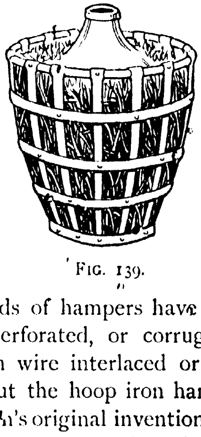
FIG. 139.

Since that time many various kinds of hampers have been introduced, in sheet metal, plain, perforated, or corrugated, corrugated strips, expanded metal, in wire interlaced or spot welded, and many other methods; but the hoop iron hamper, made on the broad principles of R. Leigh's original invention, still holds the field in Great Britain and Europe generally. In the meantime, the wicker carboy basket has practically disappeared.

British Railway Regulations for Transport of Carboys.

It frequently happens that glass carboys get broken, particularly in railway transit, by the jolting or shunting of railway trucks, and the acid running out is not merely lost, but often does a great deal of damage to other merchandise, and to the railway truck. In Great Britain this kind of trouble became excessive during the war period (1914 to 1919), when so many more consignments than usual were handled under very difficult railway conditions. In consequence, the British Railway Companies (under the Ministry of Transport) issued new regulations (11th August 1919), to come into force 1st January 1920, dealing with traffic in carboys, their straw packing, stoppering, luting, and loading.

(1) **Definition of term "Carboy."**—The term "carboy" means a globular bottle of not more than 12 galls. capacity, made of glass not less than about ⅛ in. thick in any part, practically free from striæ and bubbles, carefully annealed, and with the initials of the maker, or other distinguishing mark, on the neck.

NOTE.—*For liquids not exceeding* 1·2 *sp. gr. carboys up to* 14 *galls. capacity may be used.*

(2) **Straw Packing.**—Each carboy must be firmly packed in a hamper of iron or wickerwork, with a minimum thickness of ½ in. of straw packing between the hamper and the carboy. This packing must be renewed as soon as it loses its elasticity, and the hamper must be kept in good repair. The straw packing in the carboy hampers, when handed to the railway company, must be sufficiently damp to prevent fire.

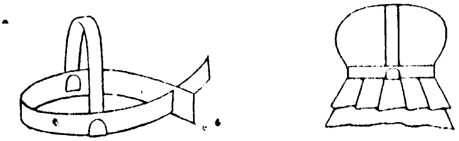

FIG. 140.

(3) **Stoppering and Luting.**—Each carboy must be provided with a good earthenware or glass stopper, and must either (*a*) be well luted with plastic (moist) clay, or (*b*) well luted first with plaster of Paris and then a layer of moist clay placed over the plaster of Paris, the stopper in all cases to be tied over with a waterproof material to keep the clay moist, and then with strong canvas firmly tied or wired round the neck of the carboy. Other equally effective means of luting may be used, provided the stopper is in all cases firmly secured and luted, so that the acid cannot escape. An effective method of securing the stopper is by means of a flat metal band, passing round the neck of the carboy and over the canvas (Fig. 140).

In the case of certain specified chemicals an effective vent in the stopper is necessary.

Carboys containing hydrochloric acid (muriatic acid or spirit of salt) may be stoppered with cork bungs luted with paraffin wax covered with canvas, the whole to be secured with copper wire or by a flat metal band passing round the neck of the carboy and over the canvas. When passing in full truck-loads the carboys may be stoppered with tightly twisted straw stoppers.

(4) **Loading.**—For traffic in full truck SINGLE TIER loads, the carboys must be placed close up to the end and side of the wagon and fastened together at all points of contact with strong cord or wire (to be provided by the senders); any space must either be battened off with substantial timber, positioned close to the shoulder of the carboys, or filled with other approved packing such as straw, sacks of straw, old hampers, etc., or, alternatively, a framework approved by the company may be fitted in the truck to support each carboy separately. The packing material or framework to be provided by the senders.

In the case of *double tier* loads each carboy must be placed on a nest of straw between the shoulders of the bottom tier carboys, the two rows of three at either end to be fastened together with strong cord or wire at each point of contact. The carboy hampers must be interlaced with rope, the ends of which must be braced to give firmness, and secured to the buffers or sheet hooks of the wagon. Wagons exceeding the height of the carboys must not be used.

NOTE.—*The Great Western Company do not carry nitric or sulphuric acid in double tier loads, and require the end hampers in single tier loads to be secured to the ends of the truck with strong cord fastened to the buffers or sheet hooks.*

In the case of *single carboys or part loads*, the carboys and hampers must be packed in substantial flat-bottomed cases, crates, or tubs. Each package must bear a distinctive label close to the mouth of the carboy:—

"THIS SIDE UP."

Carboys in boxes, crates, or tubs must not be loaded on the top of other goods, nor other goods loaded on the top of such carboys. Goods liable to be damaged in the event of breakage or leakage of the contents of the carboys must not be loaded near them.

The chief difficulty seems to have been in preventing single carboys from capsizing, or a few carboys in a truck from moving about and getting broken. Wooden cases or tubs, strong enough to carry a carboy of acid were suggested by the railway companies, but were far too costly, and also added considerably to the weight of the package, both outwards and inwards, whilst light wooden crates were altogether too weak.

The difficulty has been overcome satisfactorily, both to the railway companies and the traders, by a light, but strong, outer "safety" crate (H. Leigh, B. P. 158028 of 1921). This "safety" crate is made of deeply fluted hoop iron, and weighs only 6 or 7 lb. It is made to receive any ordinary 10-gall. carboy with its hamper, and having a base of the same diameter at the top, does not move about or overturn in railway trucks, and is also extensively used for sea-borne traffic. An additional protector for the upper part and neck of the carboy is frequently used. This top protector is also made from fluted hoop iron, and when tied down tight on to the top of the stopper covering, serves to keep the stopper and luting tight.

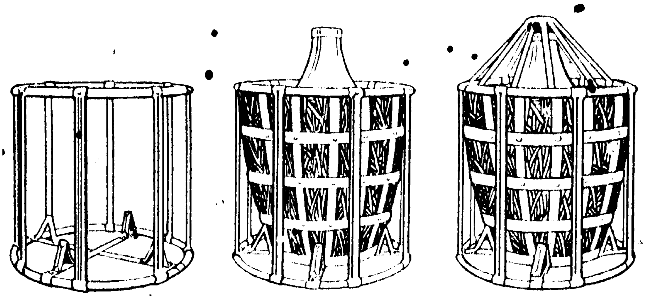

FIG. 141.

A special kind of carboy-hamper has been patented by Garneri[1] (B. P. 3196 of 1883). This basket is built up of numerous standards of wood, thin and elastic. The base is composed preferably of two conical and concentric rings, thin, and of 5 to 6 cm. (= 2 to 2⅜ in.) in diameter. The standards are bound and fixed at equal distances between the two conical rings. Wooden rings, placed at intervals in the height of the basket, are fixed both on the exterior and interior by means of a jointed mould, which gives to the basket the desired contour, according to the carboy or other article it is intended to contain.

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[1] *J. Soc. Chem. Ind.*, 1884, 3, 173.

Schleicher (Ger. P. 18172) employs tight-fitting wickerwork baskets, the upper part of which is removable and is connected with the lower part by wire fastenings. This plan is shown in Fig. 142. *b* indicates the glass, *e* the joint between the two parts of the wickerwork, e_1 the removable part of the latter, *c d* the cover.

Mauser (B. Ps. 11095 and 21986 of 1902) provides the hampers with a top kept down by springs, or suspends the carboy in the hamper by springs.

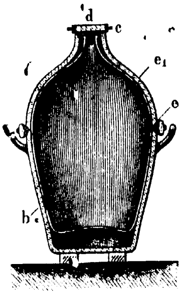

FIG. 142.

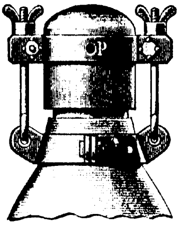

FIG. 143.

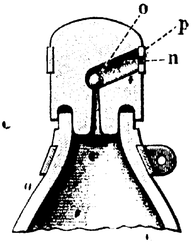

FIG. 144.

Junckers[1] employs for filling acid carboys a new kind of funnel, closed at the top. Only two openings are left; one of them for inserting the pipe or tap from the filling-vessel, the other one, provided with a neck, for conducting away any vapours formed. By making the joints with the feeding-pipe or tap and with the neck of the carboy tight by means of india-rubber washers, any loss and damage to the carboys through acid splashing about is avoided.

Mann (Ger. P. 189634) describes a contrivance for closing carboys in such a way that the channel for allowing gases to get out is not in constant communication with the outer air, but automatically opens when a certain tension has been reached, and again closes by itself when the tension is lowered. (Figs. 143 and 144 show this.) The ball *o* opens into the chamber *n*; to prevent *o* from falling out, a bandage *p* is fastened over the orifice of *n*; it possesses a small hole for the vapours to escape.

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[1] *Chem. Zeit.*, 1902, p. 582.

Contrivances for emptying Carboys.—Several contrivances have been invented for emptying acid carboys. Some of them consist of iron frames adapted for tilting, others of apparatus adapted to the carboy necks and acting on the principle of a chemist's wash-bottle, the necessary air-pressure being produced by a small force pump, or by an india-rubber bag with treadle. These and other contrivances are described by Oppler in his report on the Berlin Exhibition of Apparatus for preventing Accidents.[1] Probably the one most used at the present time is that shown in Fig. 145 after Brangwin's Patent No. 1325 of 1888.

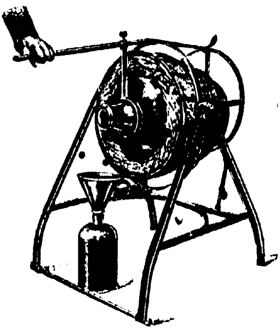

FIG. 145.

Rabe[2] describes an arrangement for running corrosive liquids from store tanks into bottles or open vessels, by means of taps. The outflowing jet is converted by radial ribs into parallel streams, and any lateral squirting is avoided thereby. In order to avoid any retention of the liquid, the ribs are made to slant towards the centre at the place where the liquid enters.

Gaden[3] (B. P. 7837 of 26th May 1915) describes a metal container fitted with a conical removable cover, which fits into the container, and is maintained in position by a bail attached to the container by means of links engaging with pivoted claws. When the bail is raised over the cover, the pivoted claws clip the latter and fix it in position. The part of the bail is fixed to the top of the cover by a spring clip, which fits into slots.

British Dyes, Ltd.[4] (B. P. 116998 of 30th July 1918), describe a stopper for carboys, and the like, but have not made any practical use of it.

The Aktiengesellschaft für Anilinfabrikation at Berlin has patented[1] (Ger. P. 8395) an apparatus for carrying acid carboys, without in any way putting stress on the handles or other parts of the hampers, so that the carboys can be handled safely, even in defective hampers.

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[1] *Chem. Ind.*, 1889, p. 528.

[2] *Z. angew. Chem.*, 1911, p. 403.

[3] *J. Soc. Chem. Ind.*, 1915, p. 1197.

[4] *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 455.

Other contrivances of this kind consist of hand-trucks and barrows, one of the simplest of which is shown in Fig. 146. It consists of a 1-wheeled barrow, the deck of which is practically level with the ground, so that one man can roll a full carboy easily on to it, and wheel it away to where required. It is manufactured by Messrs R. & H. Leigh & Sons, Ltd., Orlando Works, Bolton, to whom the author is indebted for the sketches and details given above.

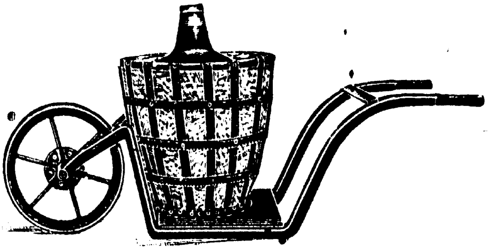

FIG. 146.

British Dyes, Ltd.[2] (B. P. 111927 of 27th December 1916), describe a 2-wheeled hand-propelled vehicle for carrying two carboys, which is very readily loaded and unloaded, and has been adopted on a practical scale.

In May 1920 the Executive Committee of the American Manufacturing Chemists' Association appointed a Special Sub-Committee to study the question of carboy closure, and their recommendations are as follows[3]:—

General Recommendations.

1. The use of clay, plaster of Paris, and other similar mixtures for sealing carboys should be discontinued. It is possible to get a good seal in this way, but the high probability

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[1] Wagner's *Jahresber.*, 1880, p. 236.

[2] *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 47.

[3] *Chem. and Metal. Engin.*, 21st March 1923; *Chem. Trade Jour.* (*Abst.*), 6th April 1923.

of getting a poor seal, the tendency of these mixtures to disintegrate during storage, the fact that a good seal is hard to remove, and results in chipped and cracked necks, the fact that such a seal is frequently used to cover up serious chips and cracks in the mouth of the carboy, and the lack of necessity for such a seal when proper gasket, porous stopper and good flat seat on the carboy mouth are used, make the use of such seals inadvisable.

2. Glass carboys used for the shipment of corrosive liquids should have an even unchipped, and uncracked surface around the lip on which to seat the gasket; this surface to be at least $\frac{1}{4}$ in. in width for carboys of 7 to 13 gallon capacity, and at least $\frac{3}{16}$ in. in width for carboys of less than 7 gallon capacity.

3. The stoppers for carboys should be required to fit fairly closely in the mouth of the carboy, and have a taper conforming closely to the taper of the inside of the mouth of the carboy.

4. The size of stoppers should be standardised as nearly as possible at not more than $\frac{1}{8}$ in. less diameter (approximately) than the inside of the carboy neck.

Stoppers and Gaskets.

5. Glass stoppers, ground to fit, should be authorised for all corrosive liquids, and should be secured in place by wire, cloth, burlap or other suitable fastening.

6. Clay or earthenware stoppers, porous, should be authorised for all corrosive liquids; they should be made of a material sufficiently porous to prevent accumulation of interior pressure under conditions of transportation or storage; they should be tough and not brittle, and of such material as will not be disintegrated by the corrosive liquid contained in the carboys. These stoppers should be of such size that the shank will fit inside the mouth of the carboy with not over $\frac{1}{8}$ in. clearance. The shank of the stopper should be at least $1\frac{1}{8}$ in. long, and should taper not more than $\frac{1}{8}$ in. on the diameter; the upper surface of the stopper should have two cross-grooves with a minimum depth of $\frac{5}{32}$ in. and maximum of $\frac{5}{16}$ in., measured at the centre of the top; provided that these stoppers, when made with screw thread to engage in corresponding threads on inside of carboy neck, need not have the grooves in their upper surface.

7. Glass stoppers (plain or screw, but not ground to fit), clay

and earthenware stoppers (not porous) and other similar stoppers should not be authorised for mineral acids or for other corrosive liquids liable to develop considerable interior pressure; such stoppers may be properly authorised under suitable conditions other than the foregoing, but which should be determined dependent on the particular article being shipped.

8. Asbestos rope, treated, should be authorised for use for any corrosive liquid that will not seriously disintegrate the gasket during use; these gaskets should be made of asbestos rope (not less than ¼ in. commercial) soaked in a mixture of 50 per cent. machine oil and 50 per cent. paraffin at a temperature of 250° F. (approximate) and subsequently wrung out slightly and allowed to cool.

9. Flat asbestos, rubberoid, and other similar gaskets (not thoroughly plastic) should not be authorised for use for mineral acids or for other corrosive liquids liable to develop considerable interior pressure; they may be properly authorised under suitable conditions other than the foregoing, but which should be determined dependent on the particular article being shipped.

10. Other gaskets having physical properties similar to the treated asbestos rope gaskets, described above, so that they will remain plastic and not disintegrate during use, should also be authorised from time to time if found to be properly efficient in transportation and storage.

Stopper Fastenings.

11. Wire fastenings of the type in which a wire is passed around the neck of the carboy just below the mouth and thence up over the stopper and twisted fast in a way to securely hold the stopper in place (such as the "Brainard" fastener) should be authorised for all corrosive liquids; the wire should be required to be made of material as highly acid-resistant as practicable ("Armco iron" is recommended), and should be not less in size than No. 14 B.W.G. They should be coated with acid-resistant paint before using.

12. Wire fasteners of the lever type (such as the "Gem" fastener) should be authorised for all corrosive liquids; the wire should be made of material as highly acid-resistant as practicable, and should not be less in size than No. 9 B.W.G. They should be coated with acid-resistant paint before using.

13. Metal screw cap fasteners, consisting of a cap to screw down over the thread on the outside surface of the mouth of the carboy should be authorised for all corrosive liquids; the thread should be required to be heavy and rounded to prevent chipping, and should be made so that, with gasket and stopper in place, at least two full threads will be engaged; these caps should be made of material as highly acid-resistant as practicable and not less than No. 18 gauge U.S. standard in thickness. The cap may be allowed to have a hole in the top.

14. "Screwed thread on stopper" fastening, in which a thread on the shank of the stopper engages in a corresponding thread on the inside of the mouth of the carboy, should be authorised for all corrosive liquids; the thread should be required to be heavy and rounded to prevent chipping, and should be made so that, with gasket in place, at least two full threads will be engaged.

Steel Drums for Transport of Sulphuric Acid.

Steel drums are used extensively for handling strong sulphuric acid. According to the Special Classification of Dangerous Goods by Merchandise Trains (Provisional Proposals) issued by the Railway Clearing House, May 1921, the specification of steel drums for the conveyance of sulphuric acid (S. 13) is as follows:—

(1) The drums must be made of the best quality mild steel sheets.

(2) All drums must be welded or riveted.

(3) Thickness of metal must not be less than 12 B.G. (2·517 mm.) for body and 10 B.G. (3·175 mm.) for ends.

(4) The ends must be flanged, let into the body of the drum from 1 to 1½ in., and strengthened by welded steel hoops, either securely shrunk on to the body of the drum, with projecting beads to cover the ends, or welded to the body of the drum.

(5) Two solid rolling hoops must be provided with well-fitting screwed steel plug and steel boss, the boss to be welded to the drum. The plug, when screwed home, must not project beyond the rolling hoops or chime.

(6) Each drum must be tested under internal pressure of 20 lb. per square inch, and proved air-tight, and this test

must be repeated whenever the drum shows signs of deterioration, and at intervals of not more than six months.

(7) The outside of each drum must be painted or varnished to preserve it.

The drums are made in various sizes, but the gross weight of the filled drum must not exceed 1400 lb.

In August 1915,[1] a lawsuit was brought in the United States by the Reid-Donald Steam Company against C. Tennant, Sons, & Co., claiming damages to the amount of £70,000 for the loss of the steamer *De Sola*, which sailed from New York to Great Britian with 7400 steel drums, each containing 800 lb. of concentrated sulphuric acid, representing about 2800 tons. After eleven days at sea, with rough weather, and with water in the hold, which had broken through the hatches, acid was found to be leaking from the drums, and two men were overcome by the fumes. The ship made for the nearest port (St John's, N.), and the cargo was taken out and the sound drums carefully restored, but after twenty-four hours at sea further leakage of acid was discovered. Soon after returning to port the ship took fire from an escape of inflammable gas, and this, together with the damage caused to the hull by the acid, caused the ship to sink.

Transport of Sulphuric Acid in Tank Wagons.—When supplying large consumers, and especially when sending great distances by land, tank wagons are employed.

Balmain and Menzies patented in 1869 this way of carrying sulphuric acid, which, however, seems to have been previously in use locally; its general use appears to date from 1880. The stronger the acid the less danger is there of any action upon the iron; but even down to 130° Tw. it can be safely carried in iron, provided there are no injurious impurities present, such as nitrous acid, and that the air has no access—the latter, because its moisture condenses on the surface of the acid, forms a layer of dilute acid, and corrodes the iron in that place.

The iron acid tanks are sometimes made of an angular section, like ordinary railway trucks; but these have been almost entirely superseded by cylindrical boiler-shaped tanks of 10 tons' capacity. A great advantage of the latter is, that they resist pressure, and that, at the consumer's works, they can be fitted with an arrangement for forcing the acid out of them into a store tank on the premises, so that the tank wagons are at once emptied and can be sent back to the seller's works. Smaller tanks of this kind, say holding 2 or $2\frac{1}{2}$ tons, can be used for road traffic.

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[1] *Chem. Trade J.*, 1915, **57**, 152; *J. Soc. Chem. Ind.*, 1915, p. 350.

Norrenberg[1] gives special instructions for cleaning out tank wagons used for sulphuric acid.

Iron tank wagons can be used for concentrated acid as well as for chamber acid. The thickness of the plate for acid down to 140° Tw. is generally $\frac{3}{8}$ to $\frac{7}{16}$ in., for chamber acid $\frac{5}{16}$ in. The plates must be very well riveted together and tightly caulked, as any leakage of acid will cause a strong corrosion on the outside, in spite of the self-evident precaution of keeping the iron very well painted with coal-tar varnish. For the same reason the tanks, when empty, must be kept tightly closed; any part temporarily exposed to the air, *e.g.*, manholes, etc., should be covered with sheet lead. The emptying takes place by means of a siphon, or else by an angular valve-tap, or by an india-rubber hose closed by a strong clamp. India-rubber, however, should be employed only for chamber acid. The valve is made of gun metal (ordinary, not phosphor bronze, which does not resist the acid so well); the iron spindle is cased with hard lead up to the screw-thread, and the stuffing-box is packed with asbestos. In spite of all precautions, a little gas is generally evolved in acid tank wagons made of iron, which, in opening them, may cause some acid to splash about and injure the men. This is avoided by a contrivance constructed by Vorster and Grüneberg.[2] On the top of the boiler tank there is a pipe, and within this another pipe, closed at bottom and open at the top. The annular space thus formed is closed at top and opened at bottom. The inner pipe has two lateral openings near its bottom through which the gas collected in the boiler tank gets into the inner pipe and thence escapes outside, whilst the acid carried along collects in the annular space between the pipes and runs back again.

Pfeffer[3] discusses tank wagons for acids in detail. Square tanks on these wagons are more easily placed on wheels, and more stable than cylindrical tanks, but in every other respect cylindrical tanks are to be preferred. The experience gained in the construction of steam boilers comes in very usefully here. Cylindrical tanks are cheaper than square ones; the ends are more easily put on; they are more easily and quickly emptied and more easily cleaned. The way of putting them on the wheels is described in detail. They are filled through the dome, in which there is an airhole, covered with fine-meshed wire-gauze in order to prevent explosions by a fortuitous taking fire of the mixture of air and gases over the acids. Directly underneath the charging hole is the discharge pipe, which is divided into two branches, each of them provided with a tap; there is also a shutting-off valve inside the cylinder, the spindle of which comes out at the dome. Sometimes diaphragms are provided in the cylinder, in order to prevent excessive oscillations of the acid in shunting, etc. The protection of the iron against the acid may be effected by a lead lining, but ebonite is preferable for this purpose.

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[1] *Chem. Ind.*, 1896, p. 553; *J. Soc. Chem. Ind.*, 1897, 16, 141.

[2] Oppler, *Chem. Ind.*, 1889, p. 528.

[3] *Z. angew. Chem.*, 1908, pp. 98-104.

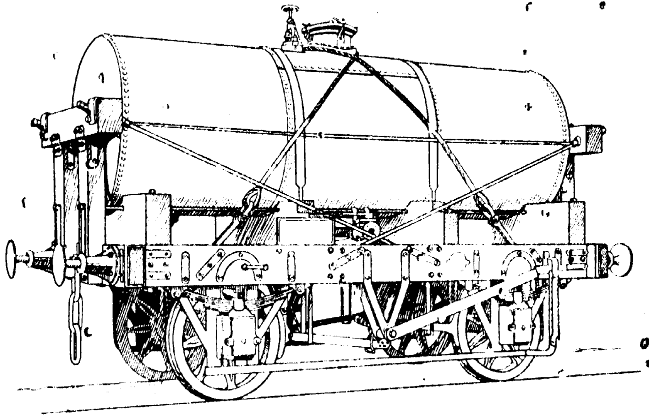

FIG. 147.

Fig. 147 shows a modern 10-ton oak-frame cylindrical sulphuric acid tank wagon, as supplied by Messrs Hurst, Nelson & Co., Ltd., Motherwell. The internal dimensions of the tank (which is built up of $\frac{3}{8}$-in. mild steel plates) are 15 ft. 3 in. long and 4 ft. 3 in. diameter, and the tank is secured to the underframe by means of galvanised wire rope fastenings. The tank is provided with a manhole cover, and with a valve and seating of regulus metal, operated from the top of the tank by a cast-iron hand-wheel through a lever and vertical spindle. There is a double arm-outlet of cast iron, to which cast-iron cocks are attached.

British Dyes, Ltd.[1] (B. P. 124997 of 7th July 1918), describe a tank wagon and its fittings, lined throughout internally with vulcanite or similar material.

Hayhurst and Messrs Guthrie & Co., Accrington, describe a tank mounted on a motor wagon. The tank is composed of an outer shell of steel, and lined internally with special ceramic material (see Fig. 148).

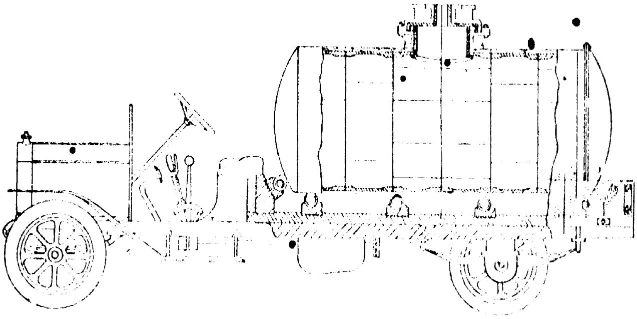

FIG. 148.

According to B. P. 122661 of 26th November 1917,[2] the joints between the tiles with which the vessel is lined are sealed with a condensation product of an aldehyde with phenol or its homologues. When the jointing is complete, the vessel is subjected to an increased temperature, to harden the jointing material. The latter may be mixed with asbestos, if desired.

According to Bulletin 184 of the Bureau of Mines, U.S.A. (p. 148), tank cars have capacities of 60,000 to 160,000 lb They are provided generally with a small pump or well into which a "blow-off" pipe dips to empty the tank as completely as possible. Sometimes a foot valve or cock is provided on the bottom of the tank for emptying, but the better practice is to blow the acid out of the tank with compressed air. The tanks are provided usually with a dome having a manhole plate; the blow-off pipe being at one side of the manhole, and the pressure air pipe at the other side, both being provided with a flanked flanged union, with a cock and a cap to protect the threads.

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 313.

[2] *J. Soc. Chem. Ind.* (*Abstr.*), 1919, p. 164.

In the 54*th Alkali Inspector's Report for* 1917, a fatality is reported, due to arseniurretted hydrogen liberated during the cleaning out of a railway tank wagon used for acid transport. After repeated washing out of the tank with water, a workman entered to remove sludge with a new galvanised bucket; conditions favouring the production of the gas were thus realised.

With reference to the removal of lead sulphate deposit from vitriol chambers, and sludge from store tanks or wagons, the 52*nd Alkali Inspector's Report* (1915, p. 15) states that free ventilation of the space should be provided for, both before entry of the men and throughout the whole period during which they are engaged on the work. It is important that it should be recognised that no material has been found effective in absorbing oxides of nitrogen that could be used in a respirator of the absorption type. Reliance on the use of such a respirator (*i.e.*, one charged with charcoal containing caustic soda) would induce a false sense of security, and might lead to disastrous consequences.

Beistle[1] gives an interesting account of the origin and work of the Bureau of Explosives, U.S.A., to promote safety in transportation of dangerous articles, such as corrosive liquids, through improvements of shipping containers, from which the following remarks are taken.

For strong sulphuric acid the tank car is very satisfactory, and the steel drum reasonably so. The glass carboy, at its best, is a fragile package. For carboys the "Stahl" packing is used frequently. This consists of four grooved vertical wooden strips, whose elasticity serves as the cushioning agent. Although initially cheap, they are destroyed by acid or fumes readily, and the cost of repairs and readjustments is high.

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[1] *J. Soc. Chem. Ind.* (*Trans.*), 1919, pp. 330-337.

Poor and insufficient cushioning cannot be cheap in the long run. It will cause accidents and increase repairs. The cushioning material should be 1½ to 2 in. in thickness all round the carboy, and should be put in carefully. A thin cushioning will give insufficient protection, and will wear through quickly by the constant rubbing of the carboy, whilst one full of lumps will cause the pressures to be brought on small areas of the carboy, and cause breakage. A 1-in. thickness does not give space for proper packing or sufficient cushioning.

In railroad transportation, observation has shown that packages receive their greatest stresses in a direction parallel to the length of the car. These stresses are due to coupling switching, and sudden stops in train operation. As far as possible, the packing serves to overcome the weakness of the package. According to Beistle, the following reported accidents occurred in the transportation of sulphuric acid for a period of five years ending 31st December 1918:—

Container.	No. of Accidents.	Persons Injured.	Property Loss.
Tank cars	14	9	$2,548
Metal drums	39	1	1,289
Carboys	1,016	30	27,261
Wooden barrels	2	...	13
Cans, bottles, jugs, etc., in wooden boxes or barrels	64	11	1,169

Regulations regarding Transport of Sulphuric Acid.

According to the Regulations for the Transportation of Explosives and other Dangerous Articles issued by the Interstate Commerce Commission, Washington, D.C. (revised) 15th July 1918 (paragraph 1855):—

Sulphuric acid must be in well-stoppered earthenware or glass vessels packed in strong barrels (Specification No. 11) or wooden boxes (Specification No. 2), or in standard carboys (Specification No. 1), or in metal drums or barrels (Specification No. 5A), or in tank cars. The inner containers must be well cushioned by excelsior, hay, straw, or equivalent packing material.

Electrolyte must be in well-stoppered earthenware or glass vessels packed in strong barrels (Specification No. 11), or wooden boxes (Specification No. 2), or in standard carboys (Specification No. 1). The inner containers must be well cushioned by excelsior, hay, straw, or equivalent packing material.

Note.—The term "electrolyte" is descriptive of a certain grade or purity of diluted sulphuric acid used in charging storage batteries. Some grades of electrolyte are so diluted that they are not classed as "corrosive liquids," while other grades are equal in strength to the stronger grades of sulphuric acid. According to paragraph 1805, corrosive liquids, which must be distinguished by a white label, include the strong mineral acids (in strength greater than one-half concentrated: *i.e.*, 47 per cent. sulphuric, 34 per cent. nitric, 20 per cent. hydrochloric acid).

Shipping Container Specification No. 1 (15th July 1918) **for Standard Glass Carboys,** reads:—

Weight.—Any glass container with a nominal capacity of not less than 10 galls. shall be classed as a carboy; and no carboy used for the shipment of acids or inflammable liquids shall have a nominal capacity of more than 13 galls.

A carboy with a capacity of 12 galls. must contain a minimum of 16 lb. of glass. A carboy with a capacity of 13 galls. must contain a minimum of 16¾ lb. of glass.

Note.—The glass in the side walls of moulded carboys should be as well distributed as practicable, and the minimum thickness should be not less than $\frac{2}{32}$ in.

Annealing.—Each carboy must be annealed for not less than thirty hours in ovens, or for not less than nine hours in lehrs, at a temperature of from 1000° F. to 1100° F., and then cooled gradually to the necessary finishing temperature required by local conditions.

Inspection.—Each carboy must be examined carefully and tested to detect any weakness or defect due to variation in thickness of glass, or other causes, and all such defective carboys must be rejected.

Marking.—An identifying mark must be blown in the bottom or neck of each carboy to enable the manufacturer's name and year of manufacture to be determined. A copy of this mark must be filed with the chief inspector, Bureau of Explosives, 30 Vesey Street, New York City. If the carboys are covered with a fibre or other composition, this mark must also be placed on the covering.

Closing.—The carboy must be closed (*a*) by having an earthenware or glass stopper inserted into the mouth of the carboy, sealed in place by clay, plaster of Paris, or similar material in a plastic condition, and securely fastened with burlap or other suitable material drawn tight and securely tied under the lip of the mouth with strong cord; (*b*) by a glass stopper with gasket, secured by metal fastenings; (*c*) by a glass stopper ground to fit, secured by burlap or other suitable material; (*d*) if the contents of the carboy are not corrosive, by a cork or other similar closing device securely fastened in place to prevent leakage.

Lead Carboys.—Any lead container of nominal capacity not less than 5 galls. shall be classed as a carboy, and no lead carboy shall have a nominal capacity of more than 11 galls.

Lead carboys shall be made with their sides and bottoms of not less than 8-lb. lead and their tops of 10-lb. lead.

The carboys must be closed with stoppers securely fastened in place to prevent leakage.

Lead carboys must be tested with 5 lb. per square inch internal pressure before each shipment, and must show no leakage under this test.

Clay or Earthenware Carboys.—(*a*) Any clay or earthenware container of not less than 5 galls. (nominal capacity) shall be classed as a carboy. No clay or earthenware carboy shall have a (nominal) capacity of more than 13 galls.

(*b*) The material in the bottom and side walls of clay or earthenware carboys shall be as evenly distributed as practicable, and the minimum thickness shall be not less than ⅜ in. The carboys shall be acid-proof.

(*c*) The carboy must be closed (*a*) by having an earthenware or glass stopper inserted into the mouth of the carboy, sealed in place by clay, plaster of Paris, or similar material in a plastic condition, and securely fastened with burlap or other suitable material drawn tight and securely tied under the lip of the *mouth with strong cord*; (*b*) by a glass or earthenware stopper with gasket, secured by metal fastenings; (*c*) by a glass or earthenware stopper ground to fit, secured by burlap or other suitable material; (*d*) if the contents of the carboy are not corrosive, by a cork or other similar closing device securely fastened in place to prevent leakage.

(*d*) Each carboy must be carefully examined and tested to detect any weakness or defect due to variation in thickness of material, or to other causes, and all such defective carboys must be rejected.

Sections 15 to 20 give particulars of the material and method of construction of wooden boxes.

Cushioning Support.—The cushioning support[1] for all carboys must be such that the type of box, when containing the carboy filled with water to the lower edge of the neck and properly packed and cushioned, must be able to withstand the following tests:—

Tests of Complete Package.

(*a*) By dropping on its bottom on to a concrete or brick floor from each of the heights of 6 in., 12 in., 18 in., 24 in., etc., in succession. Each box must withstand the first three drops without serious injury, and in testing not less than three packages the average maximum drop withstood by at least two of them without breakage of the carboy must not be less than 24 in.

(*b*) By suspending as a 14-ft. pendulum, and swinging against a concrete or brick wall with successive swings the vertical components of which are 6 in., 9 in., 12 in., 15 in., 18 in., etc. Each box must withstand the first four blows without serious injury, and in testing not less than three packages the average maximum swing withstood, by at least two of them without breakage of the carboy must be a swing with a vertical component of not less than 15 in.

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[1] If no cushioning is required, then boxed carboys shall be tested without it.

Note.—For carboys cushioned with hay or similar material, the space between the sides of the carboy and the box should be about 1½ in.

Marking.

23. The outside container must be marked: "COMPLIES WITH I.C.C. SPEC'N. No. 1," or, if desired, this marking may be indicated by a symbol consisting of a rectangle, as follows:—

I.C.C.—1.

The letters and figures in this symbol must be at least [illegible] in. high.

Shipping Container Specification No. 5a.

Iron or Steel Barrels or Drums for Acids as prescribed by I.C.C. Regulations.

Effective 1st September 1918.

1. Iron or steel barrels or drums manufactured hereafter and used for the shipment of acids as prescribed by I.C.C. Regulations, must comply with the following specifications:—

In the interpretation of the minimum thickness of metal allowed for any specified gauge, a variation, due to commercial conditions of manufacture, of not more than 2½ per cent. below the specified standard will be considered satisfactory. In figuring this variation the standard United States gauge for sheet and plate iron and steel must be used as a basis; the weights per square foot based on the United States gauges are as follows:—

4·375 lb. per square foot for No. 12 gauge.
3·125 " " " 14 "
2·5 " " 16 "

2. It is recommended that, when nature of contents will permit, each such container should be coated on the inside and outside in such manner and with such materials as will prevent corrosion.

3. Each barrel or drum having bungs projecting from the body must be provided with rolling hoops and may have them in other cases. Rolling hoops must be of the type known as solid I-bar of not less than approximately 1¼ in. by ¾ in. weighing approximately 1·406 lb. per foot, mill rolling variation

permissible; or the extra U-shaped sheet metal hoop of at least two gauges heavier than the steel in the drum. Rolling hoops formed in the metal of the body of the container are not authorised.

4. An iron or steel barrel or drum with a nominal capacity of over 55 galls. but not over 110 galls. must be constructed of metal, the minimum thickness of which in any part of the completed barrel or drum must not be less than No. 12 gauge, United States standard.

5. An iron or steel barrel or drum with a nominal capacity of over 30 galls. but not over 55 galls. must be constructed of metal, the minimum thickness of which in any part of the completed barrel or drum must not be less than No. 14 gauge, United States standard.

6. An iron or steel barrel or drum with a nominal capacity of less than 30 galls. must have a minimum thickness of metal in any part of the completed barrel or drum of not less than No. 16 gauge, United States standard.

7. Each barrel or drum must be tested under water, or with all seams covered with soapsuds or heavy oil, by interior compressed air at a pressure of not less than 30 lb. per square inch sustained for not less than two minutes, and must stand this test without leaking.

8. This type of barrel or drum must be capable of standing without leaking a hydrostatic test pressure of not less than 40 lb. per square inch, sustained for not less than five minutes.

9. When filled with water to 98 per cent. of its capacity, the type of barrel or drum must also be capable of standing without leakage a test by dropping it diagonally on its chime from a height of 6 ft. upon a solid concrete foundation.

10. Factory tests of the type package to insure that the product complies with paragraphs 8 and 9 must be made at intervals of not more than three months.

11. Provision must be made for closing the bung-holes and other openings in such manner as to prevent leakage. Bungs or other closing devices projecting beyond the chime or rolling hoops must be capable of withstanding the same test drop as prescribed by paragraph 9. Threaded metal plugs must be close fitting, and threads in the reinforcements and on the plugs must be cut at right angles to the faced surfaces thereof to

insure a uniform and solid bearing throughout the entire circumference of the gasket. Gaskets must be made of asbestos or other suitable acid resistant material.

12. The method of manufacturing the barrel or drum and the materials used must be well adapted to producing a uniform product. Leaks caused by defective manufacture of a barrel or drum must not be stopped by soldering, but must be repaired by the method used in constructing the barrel or drum.

13. The name or initials of the manufacturing company or an identifying mark, a copy of which shall be filed with the Chief Inspector of the Bureau of Explosives, 30 Vesey Street, New York, must be plainly and permanently marked on each barrel or drum.

14. Each barrel and drum must be plainly and permanently marked with the words: "COMPLIES WITH I.C.C. SPEC'N No. 5A," or, if desired, this marking may be indicated by a symbol as follows:—

$$\boxed{\text{I.C.C.—5A.}}$$

This symbol shall be understood to certify that the package complies with all the requirements of this specification.

All letters and figures in this marking must be at least ½ in. high.

Each such container of domestic manufacture shall also have plainly stamped thereon the date of manufacture thereof.

When offered for shipment the package must also bear such other description as may be required by the I.C.C. regulations for the particular article contained therein.

Transport of Sulphuric Acid in Boats.

Where the acid has to be carried on canals, etc., the barges may be arranged as tanks by lining them with lead.

As shown by Kuhlmann, jun., in 1878,[1] such boats, when used for this purpose, are subject to dangerous shiftings of the centre of gravity by the oscillation of the acid; this is overcome entirely by providing longitudinal partitions, leaving air spaces widening out at the top, as shown in Fig. 149.

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[1] *Chem. Ind.* 1879, p. 333.

Vorster and Grüneberg[1] (Ger. P. 14748) proposed the following plan especially with a view to sea carriage. Dry and finely divided kieselguhr (infusorial earth) is saturated with three or four times its weight of strong sulphuric acid. The product, which contains at least 75 per cent. of acid, retains its pulverent form, and can be transported by land or sea in lead-coated sheet-iron vessels, without any risk of breakage. When it reaches its destination, the mass is either used directly or diluted with water, and the acid is separated from the kieselguhr.

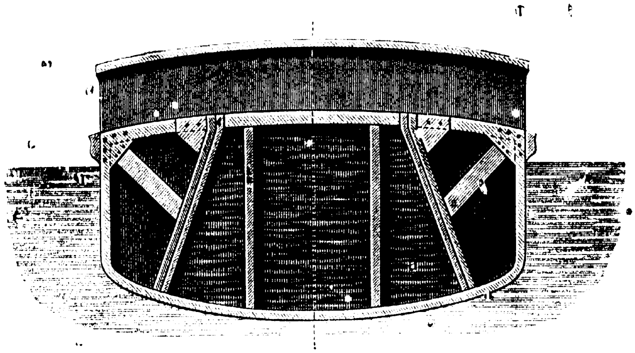

FIG. 149.

A similar idea, using clay instead of kieselguhr, has been proposed by Rippert (B. P. 8752 of 1900).

White and Rickmann (B. P. 17905 of 1887), for a similar purpose, mix sulphuric acid with anhydrous sodium or magnesium sulphate, dissolving the salt in the acid by the action of heat, and allowing it to solidify on cooling. The salt frequently does not interfere with the use of the acid, but the idea is not a practicable one.

Morris[2] (B. P. 837 of 1916) proposes sub-aqueous tanks for the transport of corrosive liquids by water. The sub-aqueous tank consists of two shells or tanks — one within the other, the inner one being eccentric with the outer. The inner tank, which carries the corrosive liquid, is stayed suitably, or braced to the outer one, so that it remains in a fixed position, and the space between the two shells is capable of being sealed, and may be filled, wholly or partially, with water or air, to determine the flotation. The tank will float in water, can be submerged, wholly or partially, as desired, by regulating the water in the outer casing. Details are given of the construction of a tank 119 ft. 6 in. long by 16 ft. beam by 13 ft. 6 in. depth, having an inner shell, 100 ft. long by 8 ft. diameter, capable of holding 250 tons H_2SO_4. The tank is lead-lined, to avoid contamination of the acid with iron.

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[1] *Wagner's Jahresber.*, 1883, p. 356.

[2] *J. Soc. Chem. Ind.*, 1916, p. 1243.

For sea transport wooden boxes lined with lead are usually employed.

According to W. G. MacKellar,[1] the boxes are made of lead, $\frac{1}{16}$ in. thick, weighing 5 lb. per square foot. Each box carries 198 lb. of acid, and there is 7 per cent. clearance space allowed for any gas that might be given off after filling. All joints are welded autogenously by means of the air and hydrogen flame. A small filling hole is cut out of the roofs of the boxes, and, after filling, the boxes are sealed finally by welding, as before, a period of two days elapsing between the filling and the final sealing, so as to allow of any gas generated to escape. The boxes are designed so as to give the maximum amount of sulphuric acid that the shipping companies will carry in one package, and are much more economical than stoneware jars, as there is always a good salvage value in the lead. The boxes are used for both arsenical and non-arsenical acid of 95 to 96 per cent. H_2SO_4, but not for higher strengths.

According to Morris,[2] some shipping companies require that sulphuric acid must be carried in small glass bottles (Winchesters), with ground glass stoppers, and that these must be packed in wooden cases in sand or whiting in sufficient quantity to absorb the acid, which would leak out if a breakage occurred. Others require that the acid should be in earthenware jars, each of about 2-gall. capacity, provided with screw stoppers and india-rubber washers, and that one, two, three, or four of these should be packed in a wooden case with whiting. Both these methods are very costly — the acid contents in some cases representing only a small fraction of the value of the package.

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[1] *J. Soc. Chem. Ind. (Trans.)*, 1921, p. 139.

[2] *J. Soc. Chem. Ind.*, 1916, p. 243.

Wheeler[1] describes the construction of charts for ascertaining the volumes of liquids contained in storage tanks and tank wagons.

Storage of Sulphuric Acid.

Vessels for storing and carrying sulphuric acid of all strengths are constructed from wood lined with lead, or from iron lined with lead; but the lead coating easily gets loose in places, and must be repaired regularly.

Hoyt[2] has patented a lead compound coating particularly adapted for the above-mentioned purposes, consisting of a thick upper layer of soft commercial lead, and a thin lower layer of an alloy of 80 to 98 per cent. lead, with 20 to 2 per cent. antimony, which is welded on to the soft lead; on rolling out, a plate is formed, the surface of which is soft and the bottom hard; this composition keeps its form better than ordinary soft lead.

Holden (B. P. 3805 of 1877) proposes to construct acid tanks from wood, which has been warmed previously and soaked in paraffin. The edges are to be made tight by a solution of gutta-percha in naphtha.

Ernst[3] describes in detail the coating of iron vessels with lead, copper, aluminium, nickel, etc.; also with india-rubber, paints, etc.

Jordan[4] (Ger. P. 280863 of 1st July 1913) coats vessels for the transportation of acids made of glass, stoneware, etc., with three layers, united by fusion, the innermost layer consisting of a mixture of bituminous and fibrous substances (jute, hair, etc.); the central one is an elastic mixture of wool, peat, etc., and the outer layer, bitumen strengthened with sand or gravel.

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[1] *J. Soc. Chem. Ind.* (*Review*), 1920, p. 141.

[2] *The Brass World*, June 1913.

[3] *Chem. Apparatus*, 1916, p. 93; *Z. angew. Chem.*, 1916, p. 370.

[4] *J. Soc. Chem. Ind.*, 1915, p. 704.

Cement vessels[1] coated with Trinidad asphalt mastic have been found suitable for storing sulphuric acid. After twelve months they showed no change, while all other materials failed.

Brookes Chemicals, Ltd., and N. Brooke[2] (B. P. 129709 of 3rd December 1917) describe the construction of acid-resisting tanks and conduits built of bricks, the outer layer of which is set in cement, followed by a layer of asphalt or bituminous material, and finally an inner layer of bricks set in and grouted with molten sulphur.

Renz[3] (Ger. P. 321029 of 13th October 1917) describes the preparation of an acid-resisting material impervious to water. Pumice or other absorptive material is finely powdered, dried, mixed with cement, strongly heated, and then impregnated with paraffin. A tar product is then added, after which the mass is heated to promote intimate admixture of the ingredients, and cooled.

Specifications and tests for bituminous acid-proof coatings for the acid-proofing of concrete surfaces are given in the Report by The Bituminous Materials and Cement Section, U.S. Bureau of Standards.[4] According to the requirements of the conditions, either bituminous paint, enamel, or mastic is used. The surface to be coated must be clean, dry, and free from dust, and a priming coat is applied always. Paints are made from bitumen or coal-tar pitch, thinned with solvents, the priming material being thinner than the paint. Enamels are mixtures of bitumen of high melting-point thoroughly incorporated with 15 to 40 per cent. of finely divided silicious filler; they contain so much bitumen that they melt below 177° C., and are applied hot. Mastics are mixtures of lead asphalt, ground with asbestos and finely powdered silicious filler; when ready for application the mixture contains 15 per cent. of asphaltic binder, 20 per cent. of mineral filler, and 65 per cent. of properly graded coarse sand. Mastics are applied hot, when the priming coat of thinned asphalt has dried to a tacky condition. Several layers of about

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[1] *Eng. and Min. World*, 28th March 1914.

[2] *J. Soc. Chem. Ind.* (*Abstr.*), 1919, p. 670.

[3] *J. Soc. Chem. Ind.* (*Abstr.*), 1920, p. 659.

[4] *Chem. and Met. Eng.*, 1920, pp. 287-289; *J. Soc. Chem. Ind.* (*Abstr.*), 1920, p. 664.

$\frac{1}{32}$ in. each are poured on and spread out with a trowel, and applied one over another, so as to give a final thickness of at least 1 in.

Marino and Bower[1] (B. P. 130302 of 29th April 1918) coat iron or steel electrolytically with lead, by employing the cleaned article as cathode in a mixture of solutions of ammonium tartrate and a soluble lead salt (*i.e.*, lead acetate), to which is added sufficient caustic soda to form a clear solution, and salicylic acid to the extent of about 5 per cent. of the weight of lead salt.

Chance & Hunt, Ltd., A. E. Holley, and H. W. Webb, Oldbury[2] (B. P. 110258 of 20th January 1917), describe an acid-resisting cement which is designed to set in two stages. The first set occurs at the same speed as the initial set of ordinary mortar, and enables ordinary building operations to be carried on at any desired speed. The second set, which corresponds to the final hardening of ordinary mortar, gives a stone-like acid-resisting product when perfectly dry.

The cement is made by adding 0·5 to 5 per cent. of plaster of Paris to a silicious acid-resisting cement of the ordinary type. Suggested proportions are:—

8	parts by weight	ground stoneware (passing No. 30 sieve).
7	„ „	fine Leighton sand.
2	„ „	ground blue brick (passing No. 60 sieve)
0·12	„ „	plaster of Paris.
3	„ „	ground silicate solution 60° Tw.

The dry solids are first mixed intimately together, and then the sodium silicate is incorporated, preferably in an edge runner mill. The cement should be used within an hour of making, and the finished work should be heated to 100° for several days, until thoroughly dry. These cements are stated not to be affected by mineral acids over a wide range of temperature, nor by sulphur dioxide, trioxide, nitrous gases, chlorine, or hydrogen sulphide. The addition of 1·5 per cent. of lead carbonate or basic lead carbonate renders the cement more quick-setting[3] (B. P. 119966 of 12th January 1918).

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[1] *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 727.

[2] *J. Soc. Chem. Ind.*, 1917, p. 1237.

[3] *J. Soc. Chem. Ind.* (*Abstr.*), 1918, p. 768.

Baskerville[1], describes the preparation of lead-coated iron, employing antimony as a binder. Mild steel sheets, after pickling in sulphuric acid, are washed, and then blackened by an antimony chloride solution, washed again, and, while still wet, dipped through zinc chloride flux into molten antimony (12 per cent.), then into molten lead, and finally quenched in oil.

A process for forming a binder on cast iron upon which pure lead can be cast and moulded, involving the use of hydrofluoric acid, is covered in the application for U.S. P. 847323 of 1920.

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[1] *J. Ind. and Eng. Chem.*, 1920, p. 152.

CHAPTER X

APPLICATIONS OF SULPHURIC ACID, AND STATISTICS

THE principal applications of sulphuric acid are the following:—

1. In a more or less *dilute* state (say from 144° Tw. downwards): For making superphosphates, sulphate of ammonia and other artificial manures.

From the statistics on fertilisers published by the International Institute of Agriculture,[1] it is possible to calculate the pre-war consumption of sulphuric acid in the production of the above-mentioned class of fertilisers as follows:—

	Metric Tons.
World production of sulphuric acid	5,000,000
European production of sulphuric acid	3,700,000
World production of superphosphate	7,500,000
Corresponding world consumption of sulphuric acid	3,000,000
European production of superphosphate	5,600,000
Corresponding European consumption of sulphuric acid	2,240,000
World production of sulphate of ammonia	1,057,000
Corresponding world consumption of sulphuric acid	793,000
European production of sulphate of ammonia	941,000
Corresponding European consumption of sulphuric acid	710,000
Percentage of the world production of sulphuric acid used for superphosphate	60 per cent.
Idem of the European consumption	65 „
Idem of the world production used for sulphate of ammonia	16 „
Idem of the European production	19 „

These figures show that three-quarters of the world production of sulphuric acid is completely lost in the soil.

Further applications are: for making sulphate of soda (salt-cake) and hydrochloric acid, and therefore ultimately for soda-ash, bleaching-powder, and innumerable other products; for preparing sulphurous, nitric, phosphoric, hydrofluoric, boric, carbonic, chromic, oxalic, tartaric, citric, acetic, and stearic acids; for preparing phosphorus, iodine, bromine, the sulphates of potassium, barium (*blanc fixe*), calcium (*pearl-hardening*); especially also for precipitating Baryta or lime as sulphates for chemical processes; sulphates of magnesium, aluminium, iron, zinc, copper, mercury (as intermediate stage for calomel and corrosive sublimate); in the metallurgy of copper, cobalt, nickel, platinum, silver; for cleaning (pickling) sheet-iron to be tinned or galvanised; for cleaning copper, silver, etc.; for manufacturing potassium bichromate; for working galvanic cells, such as are used in telegraphy, in electroplating, accumulators, etc.; for manufacturing ordinary ether and the composite ethers; for making or purifying many organic colouring-matters, especially in the oxidising mixture of potassium bichromate and sulphuric acid; for parchment paper; for purifying many mineral oils, and sometimes coal-gas; for manufacturing starch, syrup, and sugar; for the saccharification of corn; for neutralising the alkaline reaction of fermenting liquors, such as molasses; for effervescent drinks, mineral waters; for preparing tallow previous to melting it; for recovering the fatty acids from soap-suds; for destroying vegetable fibres in mixed fabrics; for artificial silk; generally, in dyeing, calico-printing, soap, glycerine, and vegetable oils, tanning, glue, gelatine, size, rubber refining, sewage. As a weed-killer and as a chemical reagent in innumerable cases; in medicine against lead-poisoning, in drugs, fine chemicals, and in many other cases.

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[1] See Monthly Bull. of International Review of the Science and Practice of Agriculture, July-August 1920.

2. *In a Concentrated State.*—For manufacturing the fatty acids by distillation; purifying colza oil; for purifying benzene, petroleum, paraffin oil, and other mineral oils; for drying air, especially for laboratory purposes, but also for drying gases for manufacturing processes (for this, weaker acid also, of 140° Tw., can be used); for the production of ice by the rapid evaporation of water in a vacuum; for refining gold and silver, desilvering copper, etc.; for making organic-sulphonic acids; manufacturing indigo; preparing many nitro-compounds and nitric ethers, especially in manufacturing nitro-glycerine, nitrocellulose, nitrobenzene, T.N.T., picric acid, and so forth.

3. *As Nordhausen Fuming Oil of Vitriol* (*Anhydride*).—For manufacturing certain organic-sulphonic acids (in the manufacture of alizarine, eosine, indigo, etc.); for dyes and intermediates and

explosives; for purifying ozokerite; for making shoe-blacking; for revivifying the spent acids used in the manufacture of explosives (T.N.T., nitrocellulose, etc.), and for other purposes.

According to the Departmental Committee on Sulphuric Acid and Fertiliser Trades, 1919,[1] the estimated approximate pre-war consumption of acid of the more important trades was as follows:—

	Tons 100 per cent. Acid per annum.	Equivalent Chamber Acid.
Superphosphates	300,000	450,000
Sulphate of ammonia	280,000	420,000
Bleaching powder, hydrochloric acid, alkali, and alum	186,000	279,000
Iron pickling	70,000	105,000
Recovery of grease in textile trades .	20,000	30,000
Copper sulphate	25,000	37,000
Dyeing and bleaching	25,000	37,000
Dyes	very	small
Oil refining	20,000	30,000
Explosives	30,000	45,000
Total . . .	956,000	1,433,000

The comparison of pre-war and post-war positions as regards productive capacity (100 per cent. acid per annum) shows:—

	PRE-WAR. Tons	POST-WAR. Tons
Oleum	22,000	450,000
Chamber	1,040,000	1,265,000
	1,062,000	1,715,000

i.e., a surplus of 653,000 tons, of which the Government plants produce 315,000 tons.

The following is a list of acid factories owned or leased by H.M. Government, with their output of 100 per cent. acid per annum:—

A. *Oleum Plants Erected during the War.*

		Tons per annum.
H.M. Factory, Avonmouth,	10 Grillos	89,200
" " Queen's Ferry	10 Grillos 10 Mannheims	111,500
" " Gretna	4 Grillos 8 Mannheims	53,500

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[1] *J. Soc. Chem. Ind.* (*Review*), 1918, p. 118; 1919, p. 90.

R.N. Cordite Factory, Poole, 2 Tentelew	8,900
H.M Factory, Oldbury, 2 Mannheims	4,500
„ „ Pembrey, 6 Tentelew	26,700
S. Metropolitan Gas Co., 1 Grillo	8,900
	303,200

B. *Chamber Plants Leased by H.M. Government.*

	Tons.
H M. Factory, West Gorton	6,200
Dalton Main Collieries	5,200
	11,400
Total acid under Government management	314,600

A very valuable paper dealing with the development of the sulphuric acid industry (1915-1918) has been contributed by H. J. Bailey to the Society of Chemical Industry,[1] from which we abstract the following information:—

Summary of Production and Utilisation of Sulphuric Acid in terms of 100 *per cent.* H_2SO_4.

	(1915).	1916.	1917.	1918.
Production by contact plant—	Tons.	Tons.	Tons.	Tons.
Government factories	(...)	42,177	138,859	112,178
Trade	(33,445)	63,496	82,227	54,465
Total	(33,445)	105,673	221,086	166,643
Imports	(31,332)	5,716	1,790	...
Production in chamber-acid plant	(1,050,000)	1,208,275	1,160,789	964,158
Total available	(1,114,777)	1,319,654	1,383,665	1,130,801
Quantity of chamber acid used to manufacture concentrated acid (10 per cent. loss allowed in process)	(123,500)	371,710	375,517	204,814
Concentrated-acid production (from chamber-acid plant)	(111,150)	334,540	337,965	184,333
Used as follows:—				
For explosives	(36,150)	258,540	274,689	130,[illegible]4
* For trade	(75,000)	76,000	63,276	54,219

* A sharp division between explosives and trade is extremely difficult to make, but the figures given are substantially correct.

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[1] *J. Soc. Chem. Ind.* (*Review*), 1921, pp. 246-252.

Sulphur Pyrites.

	1914.	1915.	1916.	1917.	1918.
	Tons.	Tons.	Tons.	Tons	Tons.
Shipments to United Kingdom	781,000	1,008,000	969,000	925,000	809,000
Home-mined, including coal brasses	(6,000)	(6,000)	(6,000)	7,000	21,000
Consumption for acid-manufacture	(800,000)	(800,000)	(922,000)	(871,000)	744,000
Stock in United Kingdom, 31st December (in acid-works and stores)	(150,000)	(250,000)	(200,000)	333,000	436,000

The consumption of pyrites represents about six-sevenths of the sulphur material required by the sulphuric acid industry. Prior to the war it was imported in a form containing 1 to 3 per cent. of copper.

The burnt residues from pyrites, known as "purple ore," were passed on to copper extraction works, and the resultant product rendered suitable for use in blast furnaces ("Blue Billy").

The production and use of cinders for 1917-1918 are given below:—

	1917.	1918.
Pyrites cinders produced—	Tons.	Tons.
Cuprous	...	386,000
Non-cuprous	609,000	130,000
Total	609,000	516,000
Pyrites cinders delivered for use in blast furnaces—		
From copper-extraction plants—		
Briquettes	208,000	208,000
"Blue Billy"	272,000	211,000
	480,000	419,000
Non-cuprous pyrites cinders delivered direct to iron works	45,000	66,000
Total to iron works . . .	525,000	485,000
Stocks of pyrites cinders at acid-makers' works on 31st December—		
Cuprous	153,000	130,000
Non-cuprous	99,000	104,000
Total	252,000	234,000

The above figures do not include quantities delivered under contract to sintering plants, as these were not in operation.

The production and consumption of spent oxide (1914-1919). are given below in tons:—

	1914.	1915.	1916.	1917.	1918.	1919. (Jan.-May 5 months).
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
Received at works .	105,000	110,000	119,200	145,600	107,900	48,013
Consumption . .	108,000	111,000	127,000	119,900	106,100	45,292
Stock 31st Dec. .	31,000	30,000	22,200	47,900	49,700	50,986 (31st May)

Sulphur.—A certain amount of sulphur is produced by the Chance-Claus recovery plant, but is used for industrial purposes other than acid manufacture.

The following table shows the approximate quantities of sulphur imported and used:

Imported.	1914.	1915.	1916.	1917.	1918.
	Tons.	Tons.	Tons.	Tons.	Tons.
Government . . .	Nil	5,700	34,200	52,600	67,800
Used for acid manufacture	(3,600)	(4,000)	(6,400)	44,900	34,200
Stocks, 31st Dec., in Government stores and at acid works	(1,000)	6,000	29,000	26,000	51,000

Sulphuric Acid from Chamber-Acid Plant.

In March 1917 the chamber-acid plant comprised 169 separate works, owned by 130 different firms, and the approximate number of chambers in use, or under construction or repair, was 1081; there were 353 Glover towers, and 425 Gay Lussac towers. The chamber space per lb. of sulphur consumed per twenty-four hours averaged 16·5 cub. ft. In March 1917, when the chamber-acid plant reached its highest production, the output obtained during that month represented an annual production of 1,307,000 tons.

The production of concentrated sulphuric acid was 334,000 tons in 1916, and 338,000 tons in 1917. During February 1917, the output reached approximately 9000 tons per week, which represents an annual output of 460,000 tons.

The chief industries in which sulphuric acid was consumed during 1916-1918, and the first five months of 1919, are enumerated on next page.

Sulphuric Acid from Chamber-Plant in terms of 100 per cent. H_2SO_4.

Summary of Uses.

	1916.	1917.	1918.	1919 (5 months).
	Tons.	Tons.	Tons.	Tons.
Explosives	352,131	337,765	152,193	5,712
Dyes	17,736	9,688	9,143	5,207
Accumulators	2,696	3,145	3,075	822
Alum	24,854	24,406	26,184	11,233
Bichromates	8,433	5,710	5,316	1,363
Bleaching powder	70,413	50,302	50,694	10,471
Copper and copper pickling	3,360	2,702	1,339	380
Copper sulphate	21,705	27,032	30,424	9,540
Drugs and fine chemicals	3,098	4,479	4,225	1,308
General chemicals	9,203	9,217	9,624	3,734
Chemical warfare	39	1,122	1,678	93
Hydrochloric acid	71,872	53,510	52,227	26,105
Iron pickling	54,523	28,864	28,840	25,406
Metal trades other than copper and iron	3,615	3,263	2,396	1,318
Mineral waters	2,421	490	391	1,884
Oil-refining	23,690	17,022	14,840	7,238
Paints and antimony colours	4,081	3,667	3,684	1,346
Sewage	442	307	723	1,613
Soap and glycerin	2,608	4,060	3,560	1,906
Sugar-refining	925	1,051	1,067	517
Sulphate of ammonia	253,340	230,145	231,092	116,144
Sulphates of magnesia and zinc	8,347	9,235	8,339	2,783
Sulphites and phosphates	10,717	11,009	12,504	5,015
Sundries	6,639	5,561	6,006	2,677
Superphosphates and compound manures	169,730	212,209	270,597	144,747
Tar	13,704	14,946	13,897	3,683
Textile industries	23,211	15,987	13,323	13,484
Total	1,163,533	1,086,894	957,381	406,229

Fuming Acid or Oleum.

The production and main uses are set out below, the figures given for consumption by trade being mainly of oleum used in the production of dyes, fine chemicals, and oil refining.

It should be noted that in the following table, the quantities given are inclusive of feed acid used, and therefore do not represent the acid made on contact plant from raw materials only.

Oleum (20 *per cent. free* SO_3).

	1916.	1917.	1918.	1919 (Jan. to May incl.).
	Tons.	Tons.	Tons.	Tons.
Production	183,000	307,000	288,000	7,500
Imports	5,500	1,500	...	...
Total . . .	188,500	308,500	288,000	7,500
Consumption—				
For explosives . . .	179,000	352,000	270,500	...
„ trade	6,500	11,000	18,000	12,000*
„ export	...	...	1,000	...
Total . . .	188,500	363,000	295,500	12,000
Stocks on 31st December .	11,000	16,500	9,000	4,500 (31st May)

* No separate data available.

Before 1915 it is estimated that the plant capacity for 20 per cent. oleum was about 25,000 to 30,000 tons per annum; whereas on 31st December 1918 the output capacity was 450,000 tons per annum of which approximately 300,000 tons was represented by Government plant.

The figures given on p. 364 represent the average consumption of sulphuric acid at all explosives manufacturers' works, including Government factories. It will be seen that there was a general progress towards increased efficiency.

The Alkali Inspector's Reports give the following number of registered sulphuric acid factories in England and Ireland. (No. 1 refers to lead chamber works; No. 2 refers to works concentrating acid or working by the contact process.)

1910.		1911.		1912.		1913.		1914.		1915.		1916.		1917.		1918.		1919.		1920.	
1	2.	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.		
150	90	149	89	146	89	146	90	150	93	151	112	144	130	147	137	146	138	140	116		

100 *per cent. Sulphuric Acid Consumption per lb. of Explosives made* 1916, 1917, 1918.

	1916.			1917.				1918.		
All Acid expressed as 100 per cent. H_2SO_4.	March to June.	July to Sept.	Oct. to Dec.	Jan. to March.	April to June.	July to Sept.	Oct. to Dec.	Jan. to March.	April to June.	July to Nov.
T.N.T.— Sulphuric acid, including oleum and that used for nitric acid expressed as 100 per cent. H_2SO_4, deducting acid re-concentrated	4·36	3·13	3·04	2·75	2·22	2·24	2·08	2·26	1·96	1·78
Picric acid from phenol— Sulphuric acid for sulphonation, deducting acid re-concentrated	1·93	1·81	1·79	1·50	1·46	1·34	1·26	0·78	0·58	0·57
Sulphuric acid including that for sulphonation and nitric acid, and deducting quantity re-concentrated	4·75	4·44	4·39	4·18	4·01	3·86	3·66	3·10	2·54	2·66
Picric acid from D.N.P.— Sulphuric acid, including that for nitration and nitric acid and deducting acid re-concentrated	2·90	2·40	2·67	2·58	2·00	2·14	1·96	2·44	1·85	...
Synthetic phenol— Sulphuric acid consumption, including oleum	4·55	3·99	3·49	3·55	3·21	3·08	3·12	2·86	2·30	2·42
Propellants (nitro-glycerin, gun-cotton, etc.) Sulphuric acid, including oleum and that used for nitric acid, deducting quantity re-concentrated	No data	2·29	2·14	1·94	1·71	1·70	1·64	1·51	1·45	1·55

Statistics relating to the U.S.A.

Bulletin 184 of the U.S. Bureau of Mines contains a comprehensive account of the manufacture of sulphuric acid in the United States from which we quote freely. (*N.B.*—All figures in metric tons.) The production in the United States increased gradually and steadily between 1865 and 1890, as shown by the following figures:—

Year.	Production as 50° B. Acid (62·18 per cent. H_2SO_4.)
1865	60,000 tons
1870	105,000 ,,
1875	150,000 ,,
1880	425,000 ,,
1885	600,000 ,,
1890	765,000 ,,

In the period 1890-1905 many new plants were put into operation, so that by 1900 the production was approximately 1,600,000 tons, and by 1905 was considerably over 2,000,000 tons annually. The production increased rapidly during the next four or five years, and by 1909 had increased to 2,750,000 tons. Beginning with the year 1911, the U.S. Geological Survey compiled production statistics. The figures are given below:—

Year.	Total Production as 50° B. Acid.	Total Value in Dollars.
1911	2,700,000 tons	17,369,872
1912	2,950,000 ,,	18,338,019
1913	3,575,000 ,,	22,684,526
1914	3,800,000 ,,	24,479,927
1915	4,170,000 ,,	32,657,051
1916	6,300,000 ,,	73,514,126
1917	7,200,000 ,,	87,640,181
1918	*7,450,000 ,,	(c) †

* From the Records of the War Industries Board.
† Not determined.

Ingalls[1] estimated that of the approximately 1,600,000 tons of acid 50° B. (62·18 per cent. H_2SO_4) made in 1900, 800,000 tons, or nearly 50 per cent. was used in fertilisers, and 320,000, or 20 per cent. was used in oil refining, the remaining 480,000 tons being used for pickling steel and for manufacturing other acid and chemical products. By 1914 the production was more than 3,500,000 tons, and of this amount approximately 2,200,000 tons was used for fertilisers. No exact data is available as to the disposition of the remainder, but it is estimated that the petroleum industries required about 500,000 tons; the iron, steel, and coke industries, about 300,000; domestic explosives about 200,000; and other chemical industries, 300,000 tons. During 1915, 1916, and 1917, many new plants were built by private concerns, principally those engaged in the manufacture of munitions. The production rose rapidly, as shown by the table given above. As the increased demand was primarily for high-strength acid, many of the new plants were for the manufacture of acid in the contact process. The increase in the production of 66° B. (93·18 per cent. H_2SO_4), or higher strength acid, is given below.

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[1] *Mineral Industry*, 1906, p. 705.

Year.	Tons (66° B.) (93·18 per cent. H_2SO_4.)
1913	810,000
1914	720,000
1915	1,160,000
1916	1,930,000
1917	2,100,000
1918	2,400,000

The total manufacturing capacity on 11th November 1918 was estimated at 501,000 tons per week (basis 100 per cent. H_2SO_4), or 9,000,000 tons per year (basis 50° B.). The Government acid plants comprised 55,000 tons (basis 100 per cent. H_2SO_4) of this capacity; the plant of the explosives manufacturers comprised 58,000 tons, and the remaining 388,000 tons was the capacity of the plants owned by the commercial manufacturers of fertilisers, chemicals, and metallurgical by-products. Of the total capacity, 40 per cent. was at contact acid plants, and 60 per cent. at chamber plants.

The distribution of the factories is described by means of a map, tables, and list of the individual works, the greater number being in the Eastern and South-Eastern States. The proportion in which the various industries were using acid during the summer of 1918 is shown on next page.

Industry.	Acid used in Tons per Month (100 per cent. H_2SO_4).	Tons per Year (as 50° B.).	Percentage of total Acid used.
1. Explosives (military and domestic)	140,000	2,700,000	36·0
2. Fertilisers	111,000	2,130,000	28·4
3. Oil refineries	35,000	671,000	8·8
4. Chemicals, drugs, and ammonium sulphate	38,500	740,000	9·9
5. Steel pickling and galvanising	36,500	700,000	9·3
6. Fabrics, textiles, etc.	5,200	100,000	1·3
7. Paints, lithopone glue, etc.	5,300	104,000	1·4
8. Metallurgical products, including storage batteries	15,200	292,000	3·9
9. Miscellaneous	3,800	73,000	1·0
Total	390,500	7,510,000	100·0

This table shows (eliminating the acid used for munitions and explosives, and allowing 10,000 tons per month for domestic explosives) an indicated requirement for normal peace industries of possibly 260,000 tons per month (basis 100 per cent. H_2SO_4), or about 5,000,000 tons per year (50° B.).

Prior to the war, the consumption of acid for fertilisers was about 2,300,000 tons of 50° B. (62·18 per cent. H_2SO_4). Up to June 1919, the consumption for this purpose was 2,500,000 tons, or more than 50 per cent. of the total production.

Sulphur-bearing Material used in the Manufacture of Sulphuric Acid.

During the early years of the sulphuric acid industry, brimstone was practically the only sulphur-bearing raw material used. In 1882, 85 per cent. of the acid was made from brimstone, and in 1895 about 75 per cent. From that time on pyrites began to be used more and more, resulting by 1900 in the almost complete elimination of brimstone for acid manufacture, except in special cases. The production of acid as a by-product in the smelting of zinc ores began in 1895, a plant at La Salle, Illinois, and the practice has become almost general in the last twenty years at the zinc plants in the Illinois field. In 1907, the practice of manufacturing acid from the waste gases of a copper blast furnace was inaugurated, followed by the use of pyrrhotite in 1908. In 1914 the acid production of the country was obtained from the following sources in approximately the following amounts:—

	Tons of 50° B. Acid.	Percentage of Total.
From brimstone (approx.)	100,000	2·6
From pyrites—		
(*a*) Spanish pyrites	1,900,000	50·0
(*b*) Domestic pyrites "coal brasses" and pyrrhotite	600,000	15·8
(*c*) Canadian pyrites	300,000	7·9
From roasting zinc ores	500,000	13·2
From waste gases at copper smelters . .	400,000	10·5
Total	3,800,000	100·0

During the rapid expansion of the acid industry between 1915 and 1918, many of the new plants were built to utilise brimstone alone. In 1917 the use of brimstone was augmented still further by the partial curtailment of the importation of Spanish pyrites; brimstone being substituted for pyrites at many plants, and used also to supplement the production from plants making acid from zinc ores. In 1917 the acid was produced from the following raw materials, approximately as below:—

	Tons of 50° B. Acid.	Percentage of Total.
From brimstone	2,350,000	32·6
From pyrites—		
(*a*) Spanish pyrites	1,650,000	22·9
(*b*) Domestic pyrites "coal brasses" and pyrrhotite	850,000	11·8
(*c*) Canadian pyrites	500,000	6·9
From roasting zinc ores	1,300,000	18·1
From waste gases at copper smelters . .	550,000	7·7
Total	7,200,000	100·0

A further curtailment of Spanish imports took place in 1918, and the production of acid was obtained approximately as follows:—

	Tons of 60° B. Acid.	Percentage of Total.
From brimstone	3,580,000	48·0
From pyrites—		
(*a*) Spanish pyrites	570,000	7·6
(*b*) Domestic pyrites "coal brasses" and pyrrhotite	950,000	12·7
(*c*) Canadian pyrites	550,000	7·5
From roasting zinc ores	1,200,000	16·1
From waste gases at copper smelters . .	600,000	8·1
Total	7,450,000	100·0

The following figures show the quantity of pyrites required to operate all plants in the United States equipped with pyrites burners[1]:—

Zone.	Fines.		Lump or Furnace Size.	
	Long Tons.	Percentage of Total Fines.	Long Tons.	Percentage of Total Lump.
1 (Atlantic Seaboard) .	290,000	60·4	135,000	37·5
2	53,000	10·9	63,000	18·0
3	27,000	5·5	19,000	5·2
4	57,000	12·0	138,000	37·8
5 and 6 . . .	53,000	11·2	5,000	1·5
Total . . .	480,000	100·0	360,000	100·0

The importation of Spanish pyrites into the United States is given approximately, as follows:—

	Tons.
Prior to 1890	20,000 per annum
1890-1900	300,000 ,,
1900-1910	700,000 ,,
1910-1914	900,000 ,,
1916	1,200,000 ,,
191[illegible]	750,000 ,,
1918	270,000 ,,

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[1] Bulletin 184, p. 39.

From statistics compiled by the U.S. Geological Survey, the production of pyrites in the United States has been as follows:—

Year.	Tons.	Year.	Tons.
1911	299,904	1915	394,124
1912	350,928	1916	423,556
1913	341,338	1917	462,662
1914	336,662	1918	464,494

Canadian Pyrites.—Prior to 1910, the production of pyrites in Canada was less than 50,000 long tons per year, of which approximately 30,000 tons was shipped into the United States.

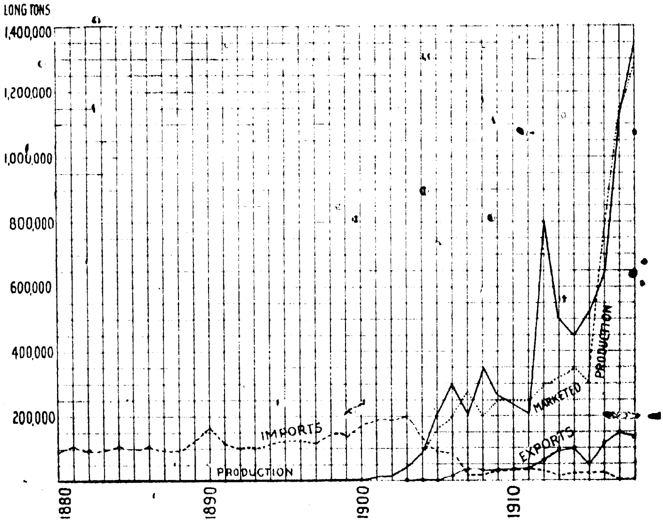

FIG. 150.—Production of Sulphur in U.S.A.

The production has increased from 80,000 tons in 1912 to about 300,000 tons in 1917. In 1917 the imports into the United States were about 180,000 tons, and in 1918 were nearly 225,000 tons. The sulphur content of the Canadian ores during the past few years has been low—averaging about 37 per cent.

Pyrites from Coal (*Coal Brasses*).—The possible yearly production of pyrites containing 40 per cent. sulphur from coal mines of the Eastern States, is estimated at 1,500,000 tons.

Smith[1] gives the graph on p. 370 showing the production of sulphur from 1880 to 1918.

Canada.—According to the Final Report of the Nitrogen Products Committee of the Ministry of Munitions, 1920, p. 110, the productions, imports, and exports of sulphuric acid (1912-1919) were as follows :—

Item.	Short Tons of 2000 lb.							
	1912.	1913.	1914.	1915.	1916.	1917.	1918.	1919.
Home production in terms of 66° B. acid = 93·19 per cent. H_2SO_4	44,651	47,227	41,919	75,838	124,920	153,530	190,621	63,596
Imports	2,486	72	166	141	2,403	216	5,954	1,437
Exports	...	1,247	3,743	9,635	1,576	9,478	5,600	[illegible]447
	Statistics compiled from official publications of Department of Mines, Canada.							

It is clear that the production of munitions of Canada has led to a substantial expansion of the sulphuric acid industry.

According to a paper on the History of Sulphuric Acid Production in Canada presented to the Toronto Section of the Society of Chemical Industry, 26th November 1920, by J. Bowman and A. Neighorn,[2] the first sulphuric acid plant was built in Canada soon after the discovery of petroleum in 1868, by the Canadian Chemical Manufacturing Co. In 1887 the factory was burned down and rebuilt with three lead chambers, 120 x 20 x 18 ft. The second Canadian plant was built in 1870 at the Ontario Chemical Works, followed by a plant of four chambers at Brockville, Ontario.

The Nichols Chemical Co. built a large plant at Capleton, Quebec, about 1887, and in 1895 the Victoria Chemical Co. established a plant at Victoria, British Columbia, which is still in existence. In 1907 the chamber system of the Nichols Chemical Co., Capelton, Quebec, was replaced by the contact system, and other plants were established by the same Company at Sulphide, Ontario, in 1907, and Barnet, British Columbia, in 1909. These are the only contact plants in Canada at the present time.

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[1] *Mineral Resources of U.S.A.*, 1918, Part II.

[2] *J. Soc. Chem. Ind.* (*Review*), 1921, p. 230.

In 1911 the Graselli Chemical Co. erected a chamber plant at Hamilton, Ontario, which concentrates the acid to 93 per cent. by the cascade system. In 1912 the Algoma Steel Corporation of Sault St Marie, Ontario, erected a Falding high chamber plant, which is still operating. Additional plants have been built in 1915-1918 (for particulars see original paper)."

Germany.

Year.	Sulphuric Acid.	
	Importation.	Exportation.
	Tons.	Tons.
1912	98,573	75,962
1913	130,256	64,968

Year.	100 per cent. Acid produced.	Pyrites burned.	Blende burned.	Other Ores, Spent Oxide, Sulphur and Hydrogen Sulphide.
	Tons.	Tons.	Tons.	Tons.
1911	1,500,230	916,265	479,329	104,583
1912	1,649,981	981,556	554,750	79,892

Year.	Cinders obtained.	
	From Pyrites, Lead Ores, etc.	From Blende.
	Tons.	Tons.
1911	750,202	403,405
1912	809,785	470,347

Number of Sulphuric Acid Factories in Germany.

Year.	Total.	Lead Chamber.	Contact Works.	Works employing both Processes.
1911	112	86	7	17
1912	109	83	8	15

In the year 1913, eighteen new sulphuric acid factories were erected for sulphuric acid, and one for anhydride.

According to the *Z. angew. Chem.*, 11th July 1919,[1] prior to 1914 copper pyrites and zinc blende were by far the most important sources of sulphur for the manufacture of sulphuric acid. In 1912, 262,700 metric tons of copper pyrites was produced in Germany, and 1,073,635 tons was imported, 84 per cent. of which came from Spain, and the remainder from Portugal, Turkey, Norway, and France. In the year, 982,000 tons of copper pyrites (109,000 from Germany), 550,000 tons of zinc blende (410,000 from Germany), 44,500 tons of sulphur containing copper and lead ores, and 35,500 of material from the purification of coal-gas, were used in the production of 1,650,000 tons of 100 per cent. H_2SO_4, and 470,000 tons of zinc oxide was obtained among other products from the above amount of sulphuric acid.

In 1913, Germany imported 46,636 tons of sulphur, 85 per cent. of which came from Italy.

Prior to 1915, the supply of sulphuric acid in Germany was derived almost exclusively from the sulphur contained in imported pyrites, but some was obtained from the gases evolved in the roasting of zinc and lead ores.[2] When foreign supplies were cut off, deposits of pyrites at Messen and elsewhere were reopened; spent oxide was utilised more efficiently and use was made of substances like kieserite and gypsum. The pre-war consumption of elementary sulphur was about 45,000 tons per annum. Deposits of native sulphur in Germany are scarce and of low grade (10 per cent.). By reducing gypsum to calcium sulphide, and burning the hydrogen sulphide obtained to water and sulphur, 30 tons per day, was obtained in 1917-1918 at Berneburg.

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[1] *J. Soc. Chem. Ind.* (*Review*), 1919, p. 352.

[2] *Z. angew. Chem.*, 2nd March 1920; *J. Soc. Chem. Ind.* (*Review*), 1920, p. 134.

The wages per hour paid in the German Chemical Industry are given as follows[1]:—

	1914.	1917.	1918.	Dec. 1918.
	Pf.	Pf.	Pf.	Pf.
Locksmiths	47	68	85	155
Artisans in building trade .	45	64	77	130
Boiler foreman and machinists	42	56	69	127
Foreman	42	54	67	124
Laboratory hands . . .	38	56	69	118
Outdoor workers . . .	34	48	67½	113
Juvenile workers . . .	...	42	52½	65
Female workers . . .	...	37½	45½	80

According to the *Z. angew. Chem.*, 6th October 1920,[2] the number of registered chemical plants in Germany during 1919, and the total number of employees, and the percentage decrease in the number of full-time workers compared with 1918, were as follows:—

Section.	Plants.	Employees.	Full-time Workers. Decrease Percentage.
Berlin	2,518	68,393	7·31
Breslau	1,235	26,377	20·84
Hamburg	2,043	72,859	27·89
Cologne	2,562	121,537	31·85
Leipzig	2,648	125,559	12·04
Mannheim	1,325	50,615	12·80
Frankfort, A.M. . . .	1,081	51,198	2·70
Nurnberg	1,648	27,623	13·35
Totals . .	15,060	544,161	Average 16·10

In 1918 there were 15,204 plants, and the decrease of 1·95 per cent. in 1919 is ascribed mainly to the loss of Alsace Lorraine. The table following gives statistics covering the period 1913-1919.

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[1] *Chem. Ind.*, 27th January 1920; *J. Soc. Chem. Ind.* (*Review*), 1920, p. 133.

[2] *Abstr. J. Soc. Chem. Ind.* (*Review*), 1920, p. 399.

Year.	Plants.	No. of Full-time Workers.	Wages Earned (in marks).	Average Yearly Wage of Full-time Worker (in marks).
1913	15,042	277,629	351,520,206	1,266
1914	15,014	245,980	313,508,108	1,274
1915	14,914	219,646	29[illegible],21[illegible],251	1,344
1916	14,993	256,420	3[illegible]2,783,261	1,493
1917	15,129	334,851	652,877,501	1,950
1918	15,204	360,256	889,141,025	2,468
1919	15,060	294,766	1,064,782,786	3,612

The Report of the British Mission appointed to visit enemy chemical works in occupied zone gives the following figures[1]:—

Output of Sulphuric Acid in Metric Tons per Day.

	1914.	1918.
Leverkusen	340	470
Höchst	224	280
Ludwigshafen	275	410
Weiler-ter-meer	48	60

Upper Silesia.—According to *J. Soc. Chem. Ind.* (*Review*), 1921, p. 257, in 1913 Upper Silesia produced 255,589 tons of acid of 50° B. (106° Tw.), or 9·7 per cent. of the total German production, and 3137 tons of anhydrous liquid sulphur dioxide. In the first six months of 1919 and 1920, the outputs were 52,887 tons and 87,960 tons respectively.

Austria-Hungary.—In 1902 four works had introduced the contact process in Austria, and the production was about [illegible]00,000 tons (strength not given).[2] In Hungary in 1909, there were nine works producing 240,000 tons of O.V. per annum.

Year.		Importation.	Exportation.
		Tons.	Tons.
1912	Ordinary sulphuric acid	36,501	16,066
	Fuming O.V. . .	213	150
1913	Ordinary sulphuric acid	24,886	14,805
	Fuming O.V. . .	36	97

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[1] *Chem. and Met. Eng.*, September 1919; *J. Soc. Chem. Ind.* (*Review*), 1919, p. 398.

[2] *Z. angew. Chem.*, 1903, p. 215.

France.—According to *Chem. Ind.*, 1911, p. 416, the consumption of pyrites and production of acid, as calculated from the former on the basis of 45 tons = 100 tons sulphuric acid, has been:—

Year.	Pyrites consumed.	Sulphuric Acid manufactured.	Year.	Pyrites consumed.	Sulphuric Acid manufactured.
	Tons.	Tons.		Tons.	Tons.
1900	397,000	883,000	1905	518,000	1,150,000
1901	461,000	1,024,000	1906	589,000	1,308,000
1902	423,000	940,000	1907	615,000	1,366,000
1903	408,000	907,000	1908	592,000	1,317,000
1904	426,000	947,000	1909	508,000	1,130,000

According to *Chem. Ind.*, 1912, p. 78, France in 1911 manufactured 1,350,000 tons sulphuric acid (113-116° Tw.) in seventy-three acid works, mostly from pyrites; only 30,000 tons was made from zinc blende, and only two works burned brimstone.

Most of the factories worked the lead chamber process; but the Societé St Gobain, partly by the contact process of the Badische, and the Maletra and Kuhlmann Companies, by the Grillo Schroder process.

According to census taken on 1st June 1920,[1] there were in operation 98 out of 127 chemical plants (*i.e.*, 77 per cent.), and the resumption of work was increasing steadily, especially in the Nord Department, which suffered most during the war.

According to Schweiz[2] the annual output of sulphuric acid was increased from the pre-war figure of 1 million tons to 2 million tons.

Belgium.—The production of sulphuric acid in 1911 was about 300,000 tons, calculated as acid of 60° B. (142° Tw.). There were in that year twenty-six factories working with lead chambers of about 400,000 cubic metre contents.

According to *L'Ind. Chim.*, December 1920,[3] the supplies of sulphuric acid are very short, the production in the Gand district being at the rate of 40,000 tons per annum, as compared with the pre-war output of 125,000 tons.

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[1] *J. Soc. Chem. Ind.* (*Review*), 1920, p. 272.

[2] *Chem.-Zeit.*, 10th September 1919; *J. Soc. Chem. Ind.* (*Review*), p. 397.

[3] *J. Soc. Chem. Ind.* (*Review*), 1921, p. 108.

According to the *Chem. Trade J.*, 2nd July 1921, the following figures are abstracted from a Report of the U.S. Bureau of Commerce:—

	1918. Metric Tons.	1920. Metric Tons.
Sulphuric acid . . .	600,000	400,000

According to *U.S. Com. Rep.*, 2nd July 1921,[1] although the Mines et Fonderies de Zinc de la Vieille Montagne—the largest zinc company in Europe—produced only 10,000 tons of sulphuric acid in 1920, as compared with 100,000 tons in 1913, the production of sulphuric acid throughout Belgium was satisfactory. The Societé de la Nouvelle Montagne produced 19,223 tons of sulphuric acid.

Italy.—According to *Z. angew. Chem.*, 20th June 1919,[2] the production of sulphur (in metric tons) is as follows:—

Year.	Crude.	Refined.	Ground.
1910	430,360	169,093	171,570
1914	337,843	149,100	165,362
1915	358,107	116,358	140,414
1916	269,374	50,900	12,200
1917	211,847	71,585	44,320

According to "Economista,"[3] the production in 1919 was 37,750 long tons less than in 1918.

According to Molinari,[4] prior to 1915 Italy produced about 318,000 tons of sulphuric acid, about 80 per cent. of which was used in the manufacture of superphosphates, and only about 18,000 tons for explosives. In 1916 Italy consumed over 160,000 tons for explosives.

In Germany, the pyrites used is utilised efficiently (the cinders containing not more than 0·8 to 1 per cent. sulphur), and the leaden chambers produce up to 10 kilos per cubic metre of space per twenty-four hours; whereas in Italian works the cinders contain 3 to 4 per cent. sulphur, and the output does not reach more than 4 to 5 kilos per cubic metre.

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[1] *J. Soc. Chem. Ind.* (*Review*), 1921, p. 294.

[2] *J. Soc. Chem. Ind.* (*Review*), 1919, p. 293.

[3] *J. Soc. Chem. Ind.* (*Review*), 1920, p. 275.

[4] *Annali de Chimica Applicata*, 1917, pp. 13-14; *J. Soc. Chem. Ind.*, 1917, p. 107[illegible].

Switzerland.—According to *Chem. Zeit.*, 20th February 1918,[1] 12,000 tons of sulphuric acid was imported prior to 1915. A large factory is being erected at Basel.

According to *Chem. Ind.*, June 1910,[2] the imports and exports of sulphuric acid, in metric tons, were:—

	1918.	1919.
Imports	5660·5	2276·8
Exports	Nil	84·1

Russia.—Suler[3] makes the following statements on the annual production of sulphuric acid in Russia, the unit being acid of 54° B. = 120° Tw.

By the Ushkoff Works, 20,000 tons; by the Tentelew Works, 24,000 tons; in twenty-five other works, 112,000 tons. There was hardly any importation from abroad. The raw material was mostly Sicilian sulphur formerly, but now it is pyrites, which is got partly in Russia (Ural, Caucasus, Donetz), but mostly imported from Spain, Portugal, Sweden, and Norway. Most of the sulphuric acid is consumed in the Baku district for purifying crude petroleum and lubricating oils.

In 1908,[4] Russia produced 163,800 tons ordinary, and 4500 tons fuming sulphuric acid, corresponding to an increase of 66 per cent. within the last ten years. According to *Chem. Trade J.*, 1911, p. 230, there are sixty to sixty-five sulphuric acid works, including those where it is only a by-product (petroleum refineries, colour works, etc.). The annual production is about 200,000 tons. According to *Chem. Trade J.*, 1914, p. 353, the production of sulphuric acid (strength not given) in 1911 was nearly 230,000 tons, the importation 2735 tons. In 1912 the production was 256,000 tons. Eight factories worked with contact process; four of these used the Tentelew system.

According to *Chem. Ind.*, 29th June 1921,[5] the production of sulphuric acid in Soviet Russia has been as follows:—

	Intended Production. Metric Tons.	Actual Production. Metric Tons.	Percentage.
Seven Factories .	24,037	14,157	63·6

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[1] *J. Soc. Chem. Ind.* (*Review*), 1918, p. 178.

[2] *J. Soc. Chem. Ind.* (*Review*), 1920, p. 297.

[3] *Vern. V. Intern. Kong. f. angew. Chem.*, 1905, **1**, 747.

[4] *Chem. Zeit.*, 1909, p. 765.

[5] *J. Soc. Chem. Ind.* (*Review*), 1921, p. 314.

Roumania.—According to *Chem. Ind.*, 28th July 1920,[1] the two sulphuric acid factories have a total capital of £80,000; they employ a maximum of 120 men, and their annual production is valued at £32,000.

Poland.—According to *J. Soc. Chem. Ind.* (*Review*), 1921, p. 298, there are ten sulphuric acid factories in Poland. As the cost of production of sulphuric acid in Upper Silesia as a by-product of the zinc smelting industry was much lower than that made in Poland from pyrites, much acid was imported from Silesia.

Norway.—According to *Z. angew. Chem.*, 31st October 1919,[2] the output of iron pyrites in 1915 was about 530,000 tons; in 1916 it was from 200,000 to 300,000 tons, at which figure it has remained since.

According to the *U.S. Com. Rep.*, 20th April 1921,[3] the exports of pyrites, ores, etc., were 316,531 metric tons in 1920, as compared with 460,436 tons in 1913.

Sweden.—In 1911, 126,810 tons of sulphuric acid, calculated as 50° B. (106° Tw.), was produced in nine factories, one of which makes fuming sulphuric acid.

Denmark.—According to the *Z. angew. Chem.*, 2nd January 1920,[4] the wages paid in *ore* (100 ore = 1s. 1½d.) per hour to sulphuric acid workers was 46·6 in 1914, and 118·9 in April to June 1919.

Spain.—According to the *U.S. Com. Rep.*, 15th April 1921,[5] the production of sulphuric acid in 1920 was 73,379 metric tons.

Turkey.—According to the *U.S. Com. Rep.*, 28th October 1919,[6] the manufacture of H_2SO_4 in Turkey, even as a by-product, does not pay.

India.—*J. Soc. Chem. Ind.* (*Review*), 1919, p. 305. Abstracted from the Industrial Handbook of the Indian Munitions Board, 1919.

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[1] *J. Soc. Chem. Ind.* (*Review*), 1920, p. 422.

[2] *J. Soc. Chem. Ind.* (*Review*), 1920, p. 77.

[3] *J. Soc. Chem. Ind.* (*Review*), 1921, p. 282.

[4] *J. Soc. Chem. Ind.* (*Review*), 1920, p. 133.

[5] *J. Soc. Chem. Ind.* (*Review*), 1921, p. 351.

[6] *J. Soc. Chem. Ind.* (*Review*), 1920, p. 66.

In default of iron pyrites, an expensive high-grade sulphuric acid is made from Sicilian or Japanese sulphur, but a cheaper acid is likely to be manufactured from sulphur dioxide obtained in the roasting of Burmese zinc concentrates. Progress in sulphuric acid manufacture is shown by the rapid fall in the amounts of imported acid, which stood at 3196 tons, worth £36,664 in 1913-1914, and at 21 tons, worth £978, in 1917-1918; whilst the amount of imported sulphur rose steadily during the same period from 6327 tons, worth £35,894 to 9785 tons worth £111,790.

Dutch East Indies.—According to *J. Soc. Chem. Ind.* (*Review*), 1921, p. 222, the imports during 1919 included the following:—

	Metric Tons.	Value. £
Sulphur	3293	43,910
Sulphur Pyrites	9160	48,180
Sulphuric Acid—		
Commercial	914	17,462
Refined	38	1,210

South Africa.—Owing to its connection with the manufacture of explosives, the sulphuric acid industry is one of the most highly developed in the union.[1] The five firms engaged in it produce about 53,000 tons of sulphur trioxide a year, most of which they consume themselves, so that in the year 1916-1917 only 2964 tons of sulphuric acid was available for disposal.

The manufacture of ammonium sulphate requires about 2500 tons of commercial acid yearly, and the cyanide process for gold, about 1800 tons of arsenic free acid. Minor quantities are used for making superphosphates, splitting fats, etc.

Messrs Kynoch, Ltd., advertise a chemically pure acid, which conforms to the standard of the British Pharmacopœia.

According to *S.A. J. Ind.*, November 1920,[2] the imports of sulphur in 1913 and 1917 were as follows:—

	1918.	1917.
Sulphur—long tons	2,672	899
Pyrites „ „	21,903	18,465
Sulphuric Acid—lb.	291,976	67,425

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[1] *S.A. J. Ind.*, February 1919; *J. Soc. Chem. Ind.* (*Review*), 1919, p. 185.

[2] *J. Soc. Chem. Ind.* (*Review*), 1921, p. 11.

Five factories produce sulphuric acid for their own use and for trade, when supplies of pyrites and railway facilities are available. The present demand for pyrites amounts to 1650 tons per month; shortly it may be 3500 tons.

Deposits of native sulphur are known to occur in the Union, but none could be worked profitably. Railway facilities are needed for the development of the massive pyrites deposits occurring in the Areachap Copper Mines. Disseminated pyrites is plentiful in the gold-bearing rocks and in the coal mines. It is estimated that during the next year coking plants will supply about 450 tons pyrites per month. Pyritic auriferous concentrates derived from the sandstone reef, afforded a monthly supply of 400 tons pyrites in 1919, and it is thought that supplies from this source can be increased to 1000 tons.

According to the *U.S. Com. Rep.*, 12th March 1921,[1] only 7·1 tons of sulphuric acid was imported in 1919.

Australia.—According to the Final Report of the Nitrogen Products Committee, Ministry of Munitions, 1920 (p. 108), considerable quantities of sulphuric acid are manufactured in Australia.

China.—According to the *Z. angew. Chem.*, 2nd July 1920,[2] the three sulphuric acid factories which China possesses are not sufficient for her daily requirements of H_2SO_4, estimated to amount to about 1000 lb., and supplies are imported from Japan.

Japan—*The Sulphuric Acid Industry.*—The development of the sulphuric acid industry has made great progress during the last decade.[3] Whereas in 1910 the production was less than 90 long. tons, in 1915 it rose to 219,543 tons, and in 1918 to 566,607 tons. The production in 1919 is estimated at over 580,357 tons. In 1915 and 1916 the exports increased very greatly (1915, 5913 tons; 1916, 11,165 tons) largely owing to the demand from Russia; since then they have receded, and in 1919 only 2390 tons were shipped abroad. The chief countries which derive supplies from Japan are China, Dutch India, Straits Settlements, and Hong-Kong. Egypt imported a little acid from Japan in 1917 and 1918.

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[1] *J. Soc. Chem. Ind.* (*Review*), 1921, p. 179.

[2] *J. Soc. Chem. Ind.* (*Review*), 1920, p. 307.

[3] *Chem. Ind.*, 6th October 1920; *J. Soc. Chem. Ind.* (*Review*), 1920, p. 357.

Great progress was made by the Japanese sulphuric acid industry during the war, and at its close in 1918 there were thirty-eight factories, representing a total capital of £8,544,162 (yen = 2s. 0½d.) and employing 2113 workmen. The output from 1914 to 1918 was as follows:—

	Long Tons.	£
1914	211,118·3	309,439
1915	219,654·8	484,375
1916	348,850·7	1,117,021
1917	546,776·0	1,520,584
1918	569,830·6	2,003,167

In 1918 the production consisted of 120,387 tons of chamber acid, 26,741·3 tons acid of 160° Tw., 16,688 tons of 164° Tw., and 40,810 tons acid of 168° Tw. The raw materials used in that year included: Pyrites 327,006 tons (25,535 tons zinc blende), nitre 5177 tons, and coal 33,271 tons. The home consumption of the acid amounted to 499,900 tons of which 9800 tons was used for making Glauber's salt, 500 tons for soda ash, 14,800 tons for caustic soda, 72,800 tons for ammonium sulphate, 270,400 tons for superphosphate, 5900 tons for nitric acid, 5300 tons for sodium sulphide, and 120,400 tons for petroleum refining, dyestuffs, and celluloid. Values and quantities of the exports during the period 1914-1919 are given below:—

	Long Tons.	£
1914	2,015·9	14,455
1915	7,884·4	51,698
1916	14,886·3	156,315
1917	4,136·4	51,866
1918	3,489·3	42,170
1919	3,153·3	44,908

In 1919 China took 33·5 per cent. of the exports of sulphuric acid; Dutch East Indies, 25·9 per cent.; Straits Settlements, 16·9 per cent.; Hong Kong, 11·9 per cent.; Philippines, 5·9 per cent.; Manchuria, 33·5 per cent.; Siberia, 0·9 per cent.; and Siam, 0·3 per cent. At present the demand is very limited, and output has to be reduced; China, which took over 4464 tons in 1920, is the only market remaining unchanged. The price of the acid varies from 1·2 to 6 sen per lb. of acid of 106 to 168° Tw., or slightly more than double the pre-war price (sen = 0·245d. at par, now about 0·311d.).

The chief deposits of sulphur in Japan occur on the Island of Hokkaido, those on the Islands of Hondo and Kyushyu being less extensive. The output of sulphur diminished considerably in 1918; the total production for that year was 64,711 tons, valued at 2,532,425 yen, representing a decrease of 45·2 per cent. in weight, and 46·9 per cent. in value, compared with 1917.[1]

According to *Chem. and Met. Eng.*, 1920, p. 1162, the following table gives some idea of the sulphuric acid industry in Japan:—

Year.	Production in lbs.	Yen.
1912	218,460,500	2,118,960
1913	413,613,100	3,328,950
1914	472,905,000	3,004,220
1915	492,026,600	4,702,660
1916	781,425,520	10,844,860
1917	741,039,160	8,916,830
1918	1,269,200,000	14,250,000
1919	1,300,000,000 (estimated)	...

Fuming sulphuric acid is manufactured in Japan by the Tentelew process at the Tokyo Sulphuric Acid Co., and at the Government Arsenal.

Argentine.—According to *Chem. Zeit.*, 1913, p. 713, Argentine possesses only one sulphuric acid works, which produces 1500 tons per annum. The importation of sulphuric acid in 1911 was 1612 tons.

According to *U.S. Com. Rep.*, 2nd November and 2nd December 1920,[2] three firms manufacture sulphuric acid (53 to 66° B. = 116 to 168° Tw.), using sulphur from Italy (by preference), Chile, and United States. Chemically pure sulphuric and hydrochloric acids are produced, but only commercial nitric acid.

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[1] *J. Soc. Chem. Ind.* (*Review*), 1919, p. 329.

[2] *J. Soc. Chem. Ind.* (*Review*), 1921, p. 36.

Brazil.—According to *J. Soc. Chem. Ind.* (*Review*), 1919, p. 444, the imports of sulphuric acid into Brazil in tons were as follows:—

	1918. Tons.	1916. Tons.
Germany	470	...
Belgium	31	...
U.S.A.	1	126
France	10	...
United Kingdom	121	11
Holland	151	...

Uruguay.—According to *Board of Trade J.*, 3rd June 1920,[1] a law was passed in 1918 authorising the Executive to borrow 100,000 pesos (peso = 4s. 2d.) for the establishment of a sulphuric acid factory at Monte Video. A site and building have been acquired, and the necessary plant has been installed.

Chile.—According to *Chem. Ind.*, 1913, p. 403, Chile possesses one factory at Coquimbo in Guyacan, which in 1911 produced 2197 tons H_2SO_4.

World's Consumption and Production.

The world's consumption of sulphuric acid in 1910 is estimated by Caspari[2] in tons (strength not given, but presumably 100 per cent. H_2SO_4).

	For Superphosphates.	For other Purposes.	Total.
Great Britain	350,000	650,000	1,000,000
Germany	530,000	850,000	1,380,000
U.S.A.	1,120,000	480,000	1,600,000
France	650,000	250,000	900,000
Italy	320,000	80,000	400,000
Austria	87,000	213,000	300,000
Belgium	155,000	95,000	250,000
Russia	35,000	115,000	150,000
Japan	...	...	80,000
			6,060,000

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[1] *J. Soc. Chem. Ind.* (*Review*), 1920, p. 258.

[2] *Chem. Trade J.*, 1914, p. 234.

Duisberg[1] estimates the world's production for 1910 at 5 million tons, calculated as H_2SO_4.

The world's pyrites production is estimated in metric tons as follows[2]:—

Norway	475,000
Spain	3,000,000
Portugal	600,000
U.S.A.	350,000
France	300,000
Italy	250,000
Germany	220,000
Canada	140,000
Greece	120,000
Hungary	100,000
Total	5,555,000

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[1] *Z. angew. Chem.*, 1912, p. 6.

[2] *Mining J.*, 29th May 1920; *J. Soc. Chem. Ind.* (*Review*), 1920, p. 292.

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